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Chlorolysis Applied to the Conversion of Chlorocarbon Residues

Hoechst-Uhde Corp, Englewood Cliffs, N J

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

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Chlorolysis Applied to the Conversion of Chlorocarbon Residues

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ABSTRACT

This program was initiated with the objective of determining the technical feasibility and economic viability of eliminating, within the United States, the discharge of large quantities of chlorocarbon residues which are harmful to the environment through the use of a German process (chlorolysis), which has been used commercially on almost identical residues, to produce a saleable product.

The concept is based on installing a centrally located conversion plant which would collect discharges from a number of nearby producers of chlorocarbon residues in order to reduce transportation and processing costs to a minimum and thereby increase the economic attractiveness of the plant. Based on information obtained from an earlier EPA report,[1] it appears that a commercial scale conversion plant could be located in either the Houston or New Orleans area where approximately one-fourth to one-third of the total amount of such residues now being produced could be converted to carbon tetrachloride. The economic evaluation shows a nominal rate of return of 24.2% after taxes based upon typical utility and consumption figures including credits for chemicals produced.

The technology selected and analyzed for this purpose is licensed by Hoechst AG (FDR) and through Hoechst-Uhde Corporation (USA) and is known as the "Chlorolysis Process." This process has been utilized in West Germany for almost a decade. A large commercial plant (50,000 MT/yr) incorporating this technology started operation last year. In addition to its established basis, "chlorolysis" also offers the advantage of handling a wide variety of chlorocarbon waste residues making it especially suitable for use in a regional plant.

This report was submitted in fulfillment of Contract Number 68-03-2380 by Hoechst-Uhde Corporation under the sponsorship of the U.S. Environmental Protection Agency. The report covers a period from December 1976 to March 1978, and work was completed as of June 1978.

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SECTION 1

INTRODUCTION

Chlorolysis is a recycling process through which by-product residues of various chlorination synthesis processes may be used as feed in order to convert them into useful industrial products, specifically, to carbon tetrachloride and hydrogen chloride.

PURPOSE

The purpose of this study is to determine the applicability of the chlorolysis process to convert toxic and undesirable chlorocarbon wastes in an ecologically satisfactory manner as well as analyze the economic basis on which such a plant can be operated in the USA. Furthermore, the process features the design of an enclosed system to handle the various potential feedstock candidates that might be expected in a regional plant.

The precedent for this study involves other studies and developments as follows:

1. Successful bench-scale tests on typical VCM waste, EPA Contract Number 68-03-2380.

2. Independent test work performed by Diamond Shamrock, EPA Contract Number 68-01-0457.

3. Commercial installations utilizing this process to produce 8,000 and 50,000 MT/yr CCl_4 at Hoechst and 36,000 MT/yr in the USSR. The 8,000 MT/yr CCl_4 pilot plant, which ran successfully for about four years, was the basis for the construction of the 50,000 MT/yr CCl_4 plant, which is now on line.

4. Survey of chlorohydrocarbon wastes by Repro Chemical Corporation, EPA Contract Number 68-03-0456.

5. The commercial application for a variety of toxic chlorinated hydrocarbon wastes (C_1-C_4) which the chlorolysis process offers.

ORGANIZATION OF STUDY

The design project report is contained in three volumes which are described as follows:

Volume I	Summary of Process and Economics
Volume II	Process Equipment and Flowsheets
Volume III	Offsites, Cost Estimates, and Standards

Volume I contains the essential information required for evaluating the process and has been prepared in accordance with NTIS requirements for public dissemination. Volumes II and III are reference volumes which include additional detailed information that provide the bases and backup for Volume I.

SECTION 2

SUMMARY

The results of this engineering design and economic feasibility study establish a basis whereby toxic and hazardous chlorocarbon wastes can be safely and economically converted into saleable end-products. Furthermore, this process offers an important advantage of eliminating the biological hazards associated with conventional alternative means of disposal, namely deep well injection, and ocean or land incineration. The process as offered is essentially a closed system and has been proven commercially. Finally, with regard to another of EPA's goals to promote resource recovery, it must be pointed out that the process conserves vital natural resources, specifically carbon and chlorine, which, instead of being destroyed, are processed into useful end products.

The economic evaluation of such an installation processing approximately 25,000 MT/yr of residues indicates a rate of return (ROR) of 24.2% after taxes (refer to Section 7). While this ROR, in itself, may not be attractive as an investment under normal chemical industry standards, it must be recognized that this return should be adjusted to reflect the costs and negative impact on ROR associated with other means of disposal particularly the incineration of valuable materials. It is essential that proper economic recognition be given to the practical elimination of health and safety hazards which are difficult to quantify as an increment of ROR.

SECTION 3

CONCLUSIONS

1. The chlorolysis process is a commercially proven process to convert toxic and hazardous chlorocarbon wastes into useful end products.

2. A plant can be designed to attain as nearly as possible a totally enclosed system with minimal discharge to the environment.

3. The chlorolysis process eliminates the ecological and safety hazards associated with other means of waste disposal, noteably deep wells, and land or sea incineration.

4. The chlorolysis process is capable of converting low molecular weight aliphatic chlorocarbons into a saleable product and is a suitable candidate process for a regional disposal plant. The process is also capable of handling aromatic chlorocarbons up to a maximum of 5% by weight of the feedstock material on a blended basis (refer to Section 5, Chlorocarbon Survey).

5. The chlorolysis process conserves vital natural resources, e.g., methane and chlorine.

6. A regional plant which could produce 75,000 MT/yr of CCl_4 (nominal 25,000 MT/yr residues processed) is estimated to cost about $29,000,000, at present-day costs, exclusive of land, and would have a 24.2% ROR at this capacity. This rate of return is based on a toll charge for handling waste at $75/MT and a selling price for carbon tetrachloride at $300/MT (refer to Section 7).

7. Actual plant capacity should be tailored to meet specific regional requirements in order to realize optimum return consistent with previous design concepts and capacities that have been proven commercially.

8. The amount of by-product anhydrous HCl generated from the prototype design plant would not justify further processing involving separate HCl electrolysis and/or oxychlorination units, especially at present prices for HCl as muriatic acid. In the event the regional plant is located near or adjacent to such processing plants, e.g., a VCM complex, consideration should be given to the sale of anhydrous HCl as feedstock, thereby upgrading the value of the by-product HCl.

SECTION 4

RECOMMENDATIONS

1. Develop and execute a program to familiarize appropriate governmental agencies and the industrial sector with the advantages and economic features of chlorolysis for toxic chlorocarbon waste disposal.

2. Investigate incentives available in the form of subsidies, public financing, tax credits, etc., that might be made available through appropriate governmental agencies which would enhance the economic viability and attractiveness of a regional chlorolysis plant.

SECTION 5

HISTORICAL BACKGROUND

EXPERIMENTAL WORK

Recognizing the potential hazard to public health in handling hazardous chlorocarbon residues from insecticide and herbicide plants in the USA as well as to develop a method to dispose of Herbicide Orange (HO) which was used as a defoliant in the Vietnam War, EPA authorized the Hoechst-Uhde Corporation (HUC) in 1973 to undertake an experimental study to assess the applicability of the Hoechst AG chlorolysis process to convert such wastes into carbon tetrachloride. At the same time, in a parallel effort, EPA also determined that sufficient chlorocarbon residues were being generated in the USA from vinyl chloride monomer (VCM) and chlorinated solvent production alone to sustain regional, multi-industrial waste source treatment facilities.

On this basis, experimental tests were conducted on blends of typical chlorinated solvent wastes and Herbicide Orange (HO) to determine the conversion that could be expected and whether the dioxin content of the HO could be eliminated or reduced to an acceptable level. HO, which was used as a military defoliant, is a mixture of equal parts of the n-butyl esters of 2,4-dichloro and 2,4,5-trichlorophenoxyacetic acids and also contains about 14-18 ppm tetrachlorodibenzo-p-dioxin (dioxin or TCDD), a very powerful teratogen.

The tests included one blend of 32.4% HO and 67.6% distilled perchloroethylene waste which was fed into an experimental bench scale reactor operating at a reaction temperature of approximately 600°C and an operating pressure of 2500 psig. Even this feed mixture was essentially all converted to carbon tetrachloride, carbonyl chloride, and hydrogen chloride, with the measured TCDD content of the product CCl_4 under 1 ppb. The HO sulphur content of 0.04% produced a corrosion rate in the nickel reactor of 6.4 mm/yr with intercrystalline attack to a depth of 0.25 mm.

This experimental work plus information on the relative amounts of VCM wastes generated compared to those involving pesticides led to the conclusion that only approximately 5% of the total feed material to a regional chlorolysis plant should consist of wastes such as HO. Mixtures containing greater percentages would probably cause accelerated corrosion due to the more prevalent traces of sulphur in insecticide and herbicide residues. The data also strongly suggested that certain parts of any commercial chlorolysis conversion reactor should be designed as "sacrificial." That is to say, the

reactor should be segmened in the direction of reactant flow with particular attention to the segement containing the zone of maximum reaction. It is this particular segment which will undergo extra severe corrosion when extreme sulphur conditions are imposed by the feedstock. This segment, therefore, must be carefully positioned and monitored, and easily removed and replaced with a backup unit always kept on site for this purpose.

CHLOROCARBON SURVEY

The volume of chlorocarbon wastes generated in the United States was estimated to be approximately 190 MM lbs/yr (86,400 MT). Current methods of disposing of these wastes range from ocean discharge, burial, and deep well injection to open-pit burning and enclosed incineration. About 55% of these wastes are produced in the Gulf Coast area.

The identified residues are suitable feedstocks for a chlorolysis operation provided they are pretreated to remove particulates, moisture, and high boiling components.

Geographically, the chlorocarbon wastes are generated primarily at Gulf Coast locations ranging from Corpus Christi, Texas, to New Orleans, Louisiana. The apparent concentration along the Gulf Coast indicates that a regional waste disposal unit would be viable. Such a regional facility should include a chlorolysis unit, a waste pretreatment unit, and a conventional incineration unit.

In addition to assessing the volume of wastes generated, it is also necessary to consider the ultimate application and use of any product that can be realized by the conversion of this material. At the present time, chlorolysis represents a commercially proven technology capable of handling the broad range of chlorinated hydrocarbons produced from process manufacturing facilities in the chlorinated hydrocarbon field. Up to the present time, chlorolysis has only been considered for the production of carbon tetrachloride. Whether modifications could or should be initiated to diversify the product slate is currently an unresolved matter. Accordingly, the survey presented in the following paragraphs of this section of the report is confined to the carbon tetrachloride market.

The total production capacity for carbon tetrachloride is estimated to be about 540,000 U.S. tons per year (491,000 MT). However, this capacity is flexible because perchloroethylene and carbon tetrachloride are coproducts. The ratio of these products can be varied to satisfy swings in the marketplace.

About 80% of the carbon tetrachloride produced is used in the manufacture of Freon-11 and 12 for refrigeration and propellant usage. The 20% balance is used for miscellaneous applications and export.

Growth of the carbon tetrachloride market has been closely related to the growth of the fluorocarbon market. The growth of this market through 1975 had been about 6% per year. The fastest growth has been experienced by the propellant sector. This represents some 40% of the fluorocarbon market.

However, the recent concern about the depletion of the ozone layer, attributed to the C_1 fluorochlorocarbons, has reduced the use of fluorocarbon aerosol propellants by about 50%. This slowdown is expected to result in zero growth until the ozone depletion question is resolved.

The volume of carbon tetrachloride that moves into the marketplace has been reduced to about 440,000 U.S. tons. Further pressure on the aerosol market will result in the volume dropping to about 340,000 U.S. tons, where it would be expected to stabilize.

The product mix of plants that co-produce carbon tetrachloride with either perchloroethylene or methylene chloride and chloroform can adjust to compensate for these losses in the carbon tetrachloride market. Indeed, such adjustments are already being made.

A chlorolysis unit rated at 24,000 U.S. tons per year of residue feed would produce about 92,000 U.S. tons of carbon tetrachloride. This represents about 30% of the projected stabilized market. This influx of new capacity would have a significant effect on present producers. Further adjustments in product mix would be necessary as would be the closure of marginal operations.

SECTION 6

GENERAL PROCESS DESCRIPTION

INTRODUCTION

The chorolysis process includes the following plant units: pretreatment of residues, reaction, distillation, and emergency absorption. In addition, a high temperature incineration unit must be provided to eliminate any leftover residues (see Figure 1).

Residues cannot be introduced into the chlorolysis process as received, i.e., in the form they have been supplied, they must be treated. Light ends, for example, contain water which must be removed in a drying unit. VCM-residues and solvent residues are contaminated with solids such as soot, which must be removed in a falling film evaporator unit.

The treated residues are then passed to the reaction unit. Reaction takes place at high pressure and high temperature. In the distillation unit, the reaction products are separated, i.e., the HCl and carbon tetrachloride (CCl_4) from the residues, which have not been completely converted, and the excess feed chlorine. The latter two entities are then recycled to the reactor. From the gaseous HCl, a 31% hydrochloric acid solution is produced in an absorption column operating adiabatically.

An absorption unit is always available for both emergency and normal shut-down of the plant. Thus, it is possible to treat all waste gases containing Cl_2 and HCl.

All residues left over from the pretreatment as well as those waste waters containing chlorinated hydrocarbons are destroyed in the incinerator.

PROCESS DESCRIPTION

General

The following information describes a complete plant for the production of carbon tetrachloride using chlorine and chlorinated hydrocarbons as feed-stocks. Because of the wide range of possible feedstocks that can be employed, the process will have a broad technical application for the destructive removal of chlorinated hydrocarbon residues. The process was developed based on the following basic conditions:

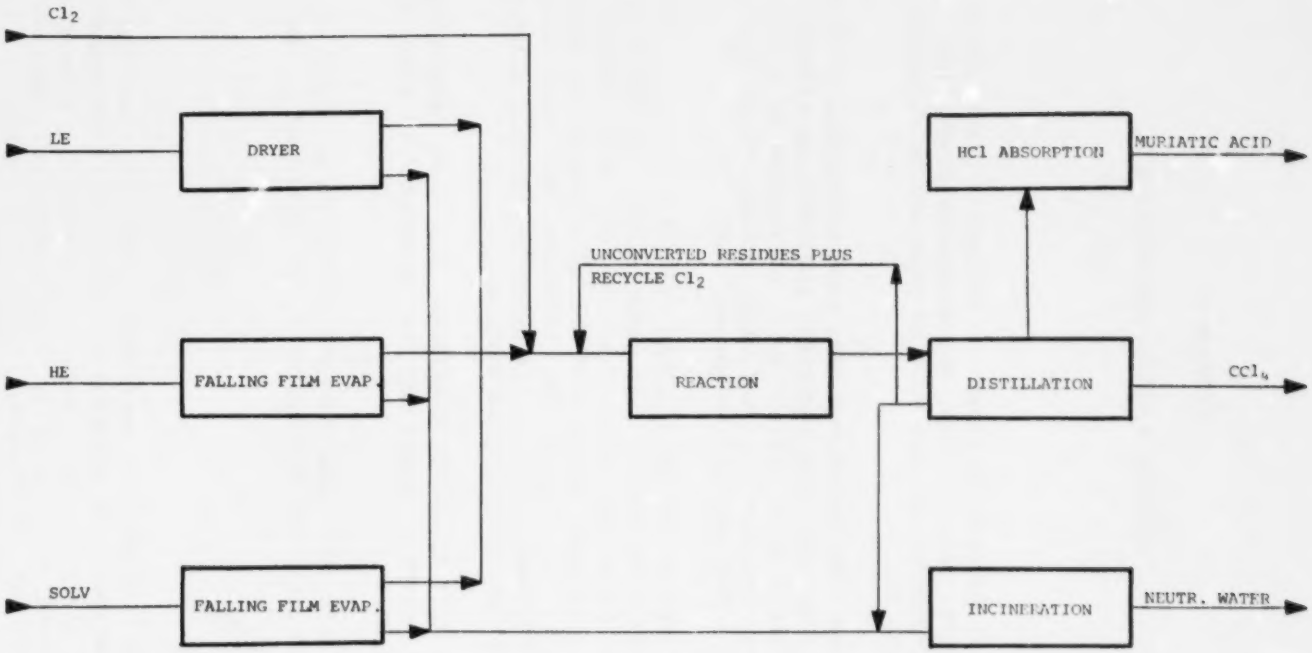

Figure 1. Block flow diagram of chlorolysis plant.

1. low consumption of chlorine and, consequently, low quantities of HCl produced;
2. maximum utilization of residues resulting from broad spectrum of industrial chlorination processes; and
3. no co-production of other chlorinated hydrocarbons.

Suitable raw materials are those residues from the production of vinyl chloride monomer, chloromethanes, propylene oxide, allyl chloride, perchloroethylene, as well as residues from benzene chlorination. The maximum content of aromatics, however, should not in general exceed 5%, calculated as benzene.

As an example, carbon tetrachloride is to be produced in an adiabatic reaction from chlorine and VCM-residues mixed with solvent wastes according to the following stoichiometric equation:

$$1 \text{ kg residue} + 2.734 \text{ kg } Cl_2 \rightarrow 3.010 \text{ kg } CCl_4 + 0.723 \text{ kg HCl} + 0.001 \text{ kg } Br_2^* \quad (1)$$

This equation is based on a typical feedstock analysis as specified in Chapter 3.

With a pressure of approximately 200 bar and a temperature of approximately 600°C, the conversion is more than 95% complete. Those heavy ends, not completely converted (chiefly hexachlorobenzene) are separated from the reaction products in the first distillation column and recycled to the reactor to extinction.

PRETREATMENT OF RESIDUES INCLUDING LIGHT ENDS, HEAVY ENDS AND SOLVENTS

Drying of Light Ends (see Figure 2)

This unit is provided for pretreatment of wet light ends with a design water content of 0.1% by weight. For the chlorolysis process, the moisture content must be reduced to less than 20 ppm by weight.

The drying unit consists of two adsorbers and one regeneration system. The wet light ends wastes are continuously fed as liquid into the unit (by means of pumps), passing through one of two adsorbers L-151 A/B from bottom to top. The dissolved water in the wastes are adsorbed on silica gel. The dried organics leave the unit and flow into intermediate tank V-203.

While one adsorber is being charged, i.e., drying, the other is being regenerated. Regeneration is achieved by activation with hot inert gas and subsequent cooling. Regeneration takes place counter-currently to the drying operation, i.e., from top to bottom. Prior to activation, the adsorber is drained and the liquid sent into separator V-152.

*from traces of bromides in rock salt.

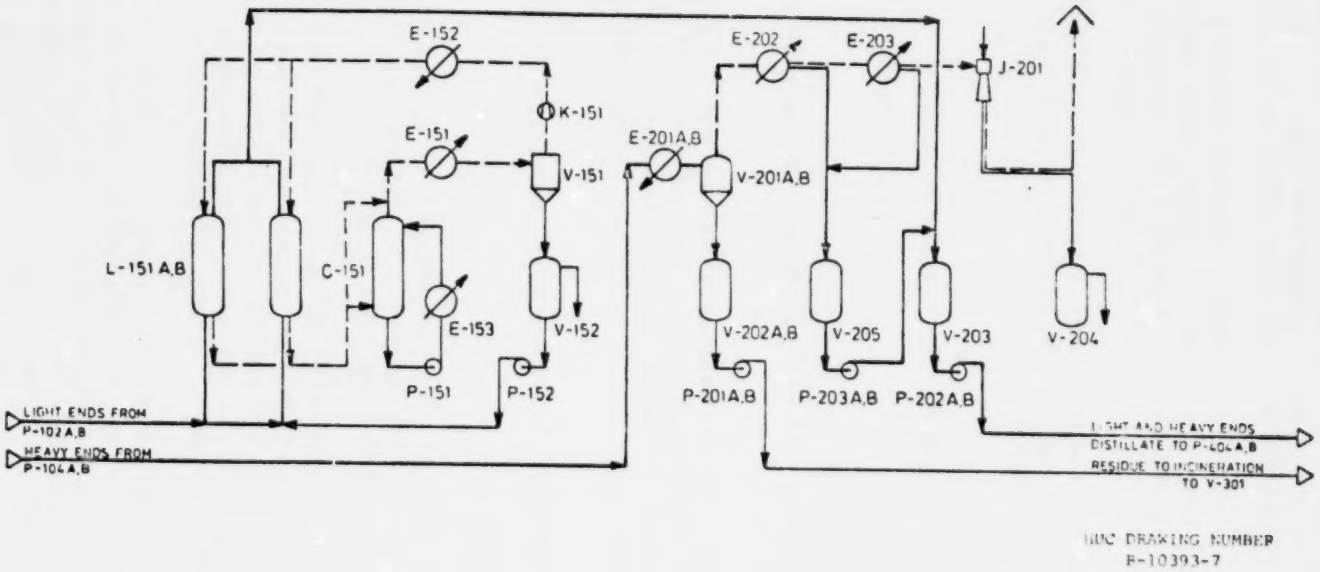

Figure 2. Drying of light ends and treatment of heavy ends.

Nitrogen is then introduced into the system as the activation gas, circulated by means of blower K-151, subsequently heated up in E-152, and eventually passed through the regenerating adsorber from top to bottom.

During the slow heating-up of the silica gel bed to about 80°C, the remaining adhering chlorinated hydrocarbons are vaporized. Scrubber C-151 is bypassed and the organics are condensed in cooler E-151, separated in V-151, and finally passed into separator V-152. When the outlet temperature of the gases rise to about 80°C, the principal quantity of chlorinated hydrocarbons have been removed and dehydration starts.

Since HCl may be formed at the higher temperatures by decomposition of the chlorinated hydrocarbons, the activation gas is passed through the NaOH-scrubber C-151 when the temperature exceeds 80°C to prevent HCl corrosion.

After scrubbing, the regeneration gas is cooled in E-151 and then passed to blower K-151. The condensed water is passed via V-151 into separator V-152. Activation is continued until the outlet temperature of the adsorber rises sharply, which indicates the end of the dehydration phase.

At about 110°C, the steam to the heater E-152 is shut off and the gas is circulated through the cooler for about 3 to 4 hours, while bypassing the NaOH scrubber C-151, until the adsorber has cooled down sufficiently.

In the heavy ends treatment unit, the waste residues are separated from tarry residues and soot by distillation.

A falling-film evaporator unit operating under vacuum (about 65 m bars) was chosen to minimize the thermal load in view of the risk of polymerization and coking.

The unit is equipped with two evaporators, because the evaporator surfaces have to be cleaned from time to time.

The heavy ends wastes are pumped via filters into falling-film evaporators E-201 A/B. Each evaporator is heated with saturated steam to approximately 120°C.

The concentrated residues are separated from the vapors in V-201 A/B and continuously drained. The residues flow via barometric leg into sealing drums V-202 A/B and are continuously pumped into residue collecting vessel V-301 or directly into the incinerator (unit 300).

The vapors are condensed in E-202 and E-203, then passed via barometric leg into sealing drum V-205 and finally pumped into drum V-203.

Vacuum required for evaporation is generated by a multistage vacuum steam jet unit J-201. Surface condensers are provided for condensation of the driving steam to minimize the production of contaminated wastewater.

The second condenser E-203 is cooled by fluorocarbon R 12 to achieve the maximum possible condensation.

Small amounts of uncondensed organic components are carried over by the condensed driving steam via the barometric leg into sealing drum V-204. From here they are passed into the incineration unit.

For corrosion protection, it is recommended that small amounts of NH_3 be fed into the suction end of the vacuum unit, thus obtaining slightly alkaline wastewater.

Treatment of Solvents (see Figure 3)

In the treatment of solvents, the residues are separated from sooty solid materials and polymers by carefully controlled distillation.

Distillation is effected in a falling-film evaporator under vacuum (approximately 0.06 bar absolute) to minimize thermal load.

Two evaporators are provided, since they have to be cleaned regularly. The solvents are transferred by pumps from tank farm through preheater E-251 into evaporator E-252 A/B. The falling-film evaporator is heated with steam to approximately 197°C. The heavies are separated from the distillate to be chlorolyzed in separator V-251 A/B and are collected in receiver V-252 A/B. By means of pump P-251 A/B, the heavies are fed directly to the incineration unit. The solvents distillat are condensed in condenser E-253, which is then cooled with warm water, and collected in pump feed vessel V-253. The distilled solvents are then passed to the reaction vessel by pumps P-252 A/B.

The warm water cycle for cooling condenser E-253 consists of circulating pump P-253 A/B, cooler E-255 and expansion vessel V-255. The vacuum required for the operation of the falling-film evaporator E-252 A/B is generated by means of steam injector J-251. A water-cooled second condenser unit E-254 is installed between condenser E-253 and steam injector J-251. Traces of uncondensed vapors from both solvents and driving steam are condensed in E-254 and collected in receiver V-254. This wastewater is then sent to the residue incineration unit.

CHLOROLYSIS PROCESS

Reaction (see Figure 4)

The chlorolysis reactions are all exothermic. The following are the equations of some characteristic oxidations, indicating the heat of reaction at 1 bar and 300°C.:

							ΔH_R (kcal/kg feed)
$CHCl_3$	+	Cl_2	→	CCl_4	+	HCl	-180 kcal
$C_2H_4Cl_2$	+	5 Cl_2	→	2 CCl_4	+	4 HCl	-1056 kcal
C_6H_6	+	15 Cl_2	→	6 CCl_4	+	6 HCl	-3770 kcal
C_6Cl_6	+	9 Cl_2	→	6 CCl_4			-483 kcal

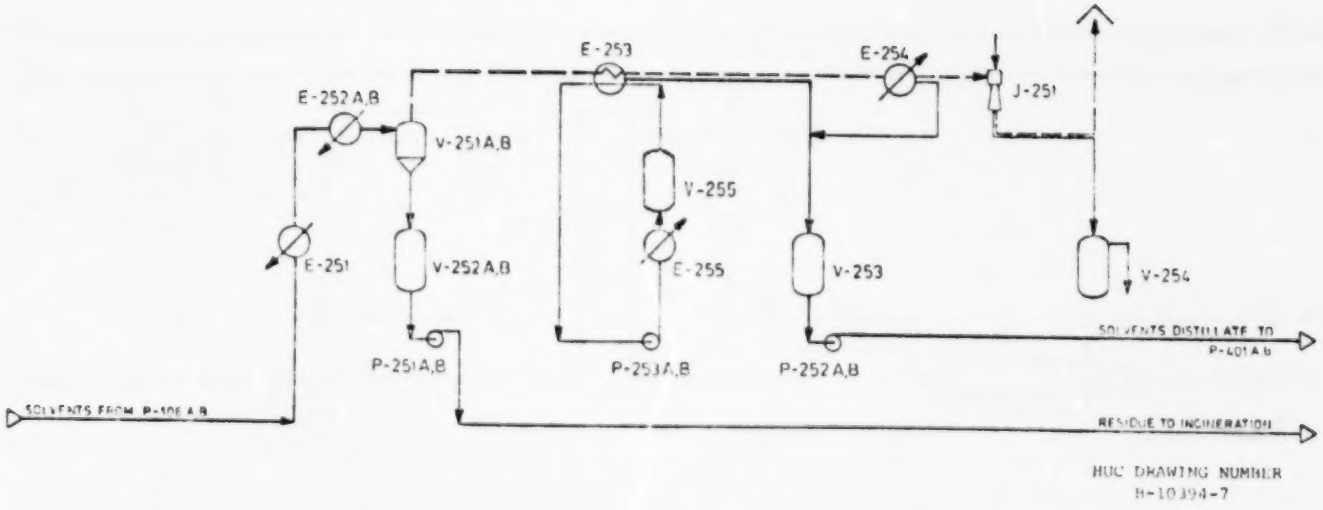

Figure 3. Treatment of solvents.

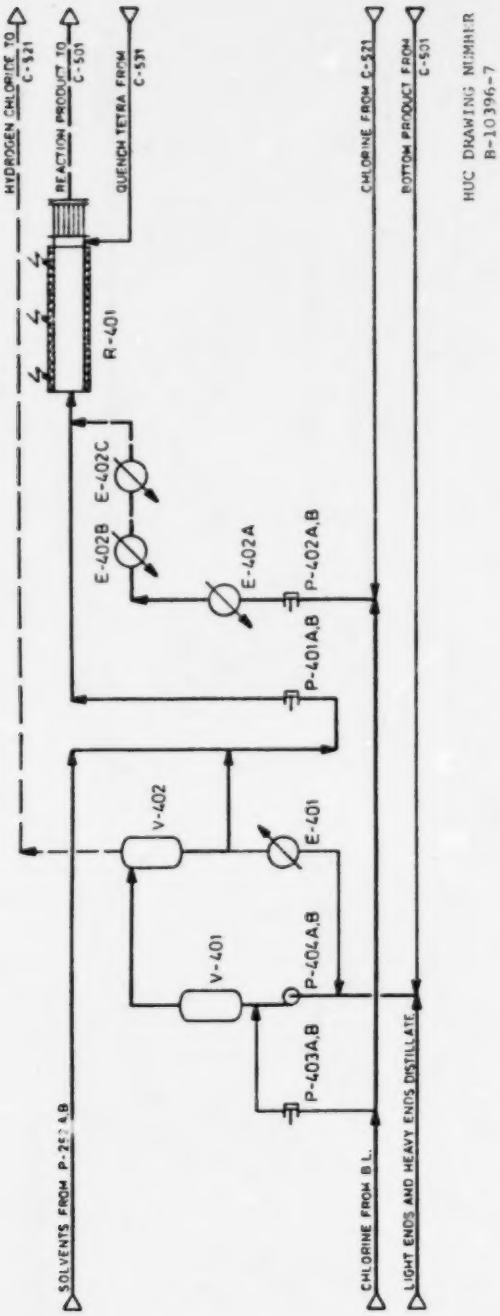

Figure 4. Reaction.

Reaction takes place at a temperature up to 600 C and 181 bars absolute. The heat of reaction is sufficient for adiabatic operation. Auxiliary heat is needed only for reactor startup. Final temperature is controlled by varying the chlorine excess in the reactor, but must not exceed 620°C, due to limitations of the materials of construction used for the reactor itself. Optimum reaction conditions vary greatly and depend on the composition of the feed residues. They are best determined by bench reactor experimentation. For example, we know that when chlorolyzing benzene and alkyl benzenes, hexachlorobenzene is formed as an intermediate which is itself only reacted above 500°C. Prechlorination of olefin-containing feedstock with cold chlorine at a temperature up to 70°C is recommended and provided in this design study, since coking products are often formed during the reaction between olefins and hot chlorine.

Therefore, liquid chlorine plus the pretreated light and heavy ends are fed into the prechlorination unit, which consists of circulating pumps P-404 A/B, holding tank V-401, separator V-402, and cooler E-401. The prechlorinated light and heavy ends are then mixed with the bottom product from heavy ends column C-501 and transferred by means of high-pressure pumps P-401 A/B into the reactor R-401.

The remaining required chlorine is fed into reactor R-401 by means of special high-pressure pumps P-402 A/B. Before entering the reactor, feed chlorine is heated to approximately 250°C by steam and Dowtherm in preheaters E-402 A/B/C. A side stream of cold chlorine is fed by pump P-403 A/B into the prechlorination unit.

Reactor R-401 consists of a nickel-lined steel tube. The outside walls of the first sections of the reactor are provided with electrical heating. Heating is required for start-up and compensation for heat losses if needed. The final section of the reactor serves to quench the reaction products by injection of carbon tetrachloride. In the quench section, the reaction products are cooled from approximately 600°C to 500°C.

By pressure relief to 22 bars absolute, reaction products are cooled down to 420°C as a result of the Joule-Thomson effect, before entering heavy ends column C-501.

Reaction by-products include hexachlorobenzene, hexachloroethane, carbonyl chloride, and carbon dioxide. Hexachlorobenzene and hexachloroethane are actually intermediate products of chlorolysis. They are concentrated in the bottom of heavy ends column C-501 and recycled back to the reactor. From compounds in the feed stock containing oxygen, e.g., water, ether, etc., carbonyl chloride, and carbon dioxide are formed. Carbonyl chloride is separated as a bottom product in the HCl column C-521 and fed into the incineration unit. CO_2 is discharged together with HCl as overhead from C-521. The small amounts of soot and iron (III) chloride (catalyst in EDC production) are discharged with hexachlorobenzene and hexachloroethane as bottom products from the heavy ends column and separated by filtration. See the following discussion and Figure 5 for details on separation and recovery system design and operation.

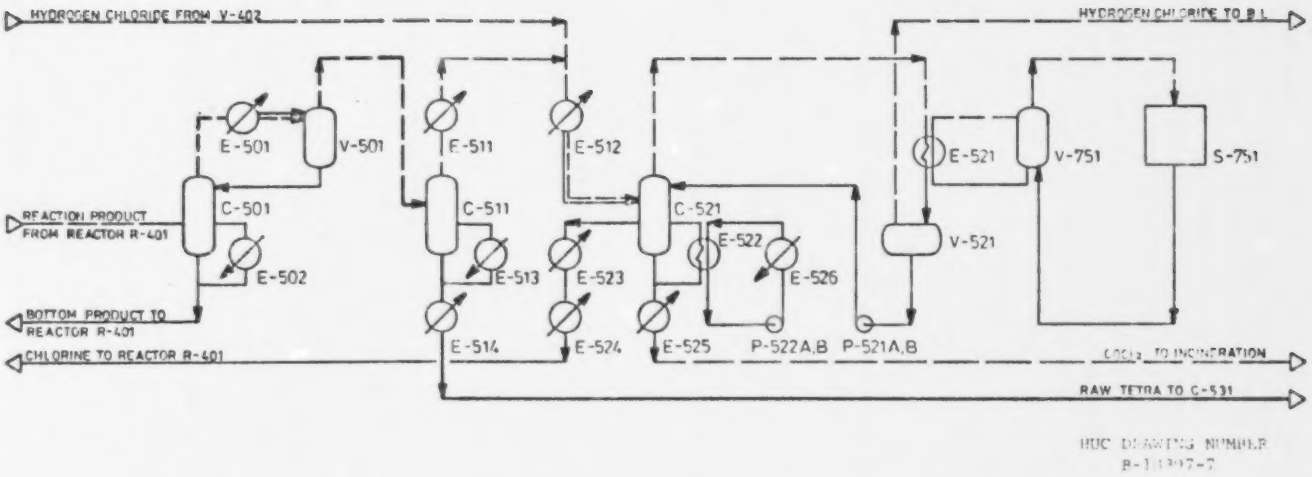

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Figure 5. Distillation I.

Heavy Ends, Raw CCl_4 and HCl-column (see Figure 5)

In the heavy ends column C-501 unconverted hexachlorobenzene and hexachloroethane are separated as bottom products and recycled to the reactor. As overhead products, gaseous HCl, Cl_2, and CCl_4, small amounts of gaseous $COCl_2$ and CO_2 are drawn off at a temperature of approximately 154°C and fed into the raw CCl_4 column C-511 for further separation. The pressure in the heavy ends column is approximately 22 bars absolute, and the bottom temperature is approximately 244°C. Dowtherm is used for heating the reboiler E-502.

The overhead products of the heavy ends column are further separated in the raw CCl_4 column C-511. Overhead products, HCl, CO_2, Cl_2, and $COCl_2$, are drawn off at approximately 69°C and fed into the HCl column C-521. The bottom product, carbon tetrachloride, containing small amounts of bromine, carbonyl chloride and traces of chlorine, hexachlorobenzene, and hexachloroethane, is drawn off and passed into the pure CCl_4 column C-531. The pressure in the raw CCl_4 column is approximately 21.5 bars absolute, the bottom temperature is approximately 225°C. The heat required for the raw CCl_4 column is supplied by a Dowtherm-heated thermosyphon reboiler E-513.

The overhead product of the raw CCl_4 column C-511 is separated in the HCl column C-521. The overhead product, HCl, is drawn off with small amounts of CO_2 and supplied to battery limits for further use.

Chlorine, still containing some carbonyl chloride, is drawn off as a side stream and recycled into the reactor together with fresh chlorine. As bottom product, a mixture of carbonyl chloride, carbon tetrachloride and chlorine is obtained, which is incinerated in unit 300. The pressure in the HCl column amounts to approximately 20.8 bars absolute. The column head temperature is approximately -8°C, whereas the column bottom is approximately 102°C.

The HCl column is heated by reboiler E-522. For its heating medium, Tripene (hexachlorobutadiene) was chosen due to its stability to chlorine. Tripene is circulated by means of pumps P-522 A/B and heated from 104°C to 160°C in heat exchanger E-526 with medium-pressure steam. The vapors from the column head are partially condensed in E-521, collected in vessel V-521, and fed by pumps P-521 A/B as reflux. V-521 is thus designed with a buffer volume surge capacity of approximately three hours of operation. If the HCl supply to the battery limits is interrupted, total condensation may take place.

Pure Carbon Tetrachloride Column (See Figure 6)

The bottom product of column C-511 is distilled into pure carbon tetrachloride in column C-531 where it is fed as liquid between the upper and middle layers of the column packings. The side stream (product carbon tetrachloride) is drawn off as a gas between the middle and lower layers of the column packings. The gas is condensed in E-531 and finally stored in intermediate tank V-531. By means of feed pumps P-531 A/B, the condensed carbon tetrachloride is fed to the shift tanks V-534 A/B, which are alternately operated. The shift tanks are discharged by pump P-534 into the final CCl_4 product tank.

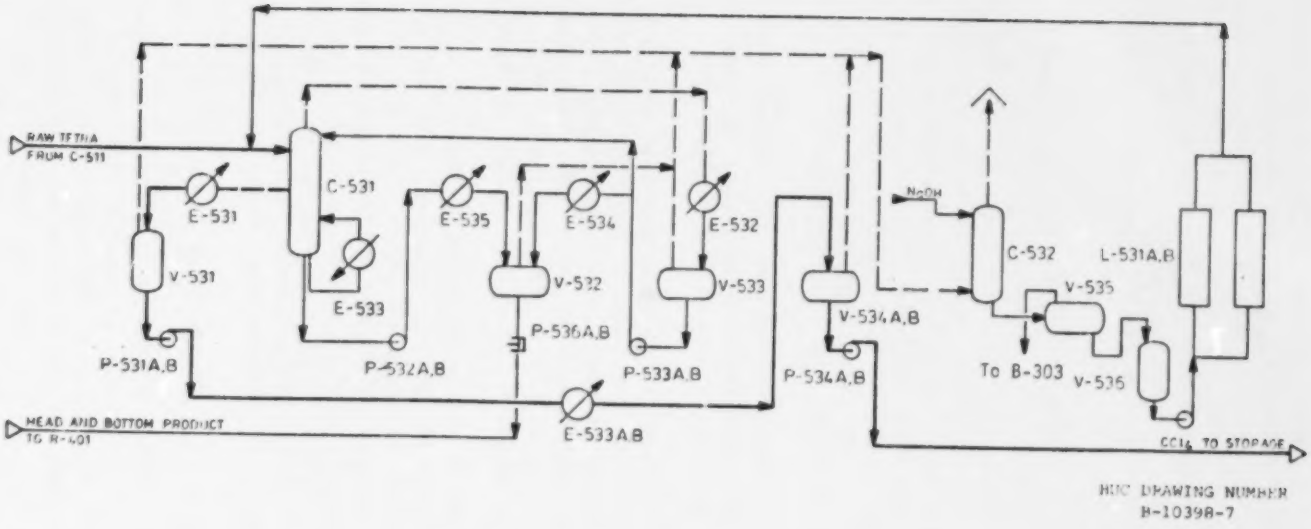

Figure 6. Distillation II.

The reboilers are heated with low-pressure steam (2 bars absolute). The bottoms are fed by means of pumps P-532 A/B via cooler E-535 into collecting tank V-532.

The overhead is condensed in E-532 and transferred into reflux drum V-533. A portion of the distillate is refluxed to column C-531. The remainder is pumped into collecting vessel V-532, mixed with the bottoms, and fed back into the quenching section of reactor R-401.

Small amounts of uncondensed vapors containing CCl_4, Cl_2, HCl and Br_2 are fed into absorber C-532 where treatment is effected by scrubbing with a 20% NaOH solution. The bottom product of C-532 is separated in V-535 into caustic wastewater and recycle carbon tetrachloride. The lighter wastewater flows via an overflow into the incineration unit. The heavier carbon tetrachloride is drawn off at the bottom of the separator, passed into vessel V-536 and then recycled to the pure carbon tetrachloride column C-531 via driers L-531 A/B.

High Temperature Unit (See Figure 7)

A high temperature unit is necessary to provide the reboiler for columns C-501 and C-511 with a suitable heating agent. The columns are operated at pressures of 22 and 21 bars, respectively; producing bottom temperatures of 250°C and 220°C, respectively. Thus, it is not economical to use steam as a heating agent.

Natural gas is used as fuel for the high temperature furnace B-701. Dowtherm serves as the heating agent for the circulating system. Pumps P-701 A/B effect the forced circulation of Dowtherm through the heater and consumer reboiler. The temperatures of the circulated Dowtherm are 305°C at reboiler supply and 275°C upon return to the furnace.

Vessel V-701 serves as collection vessel for the whole Dowtherm system, including piping and apparatus. Inside the collection vessel, a steam heating coil prevents solidification of the Dowtherm. Pump P-702 is provided to fill the system.

Emergency Absorption (See Figure 7)

The emergency absorption unit is provided for the treatment of waste vent gases containing chlorine, hydrogen chloride, and carbonyl chloride. These waste gases occur due to release of safety valves during shut-down of the plant as a consequence of the pressure release in the columns and subsequent purging with nitrogen, and also after pressure release and purging during a change of filters. The absorption takes place in liquid injection scrubbers by recirculating 20% NaOH according to the following reaction equations:

$$HCl + NaOH \rightarrow NaCl + H_2O;$$

$$Cl + 2\,NaOH \rightarrow NaOCl + NaCl + H_2O;$$

$$COCl_2 + 4\,NaOH \rightarrow Na_2CO_3 + 2\,NaCl + 2\,H_2O.$$

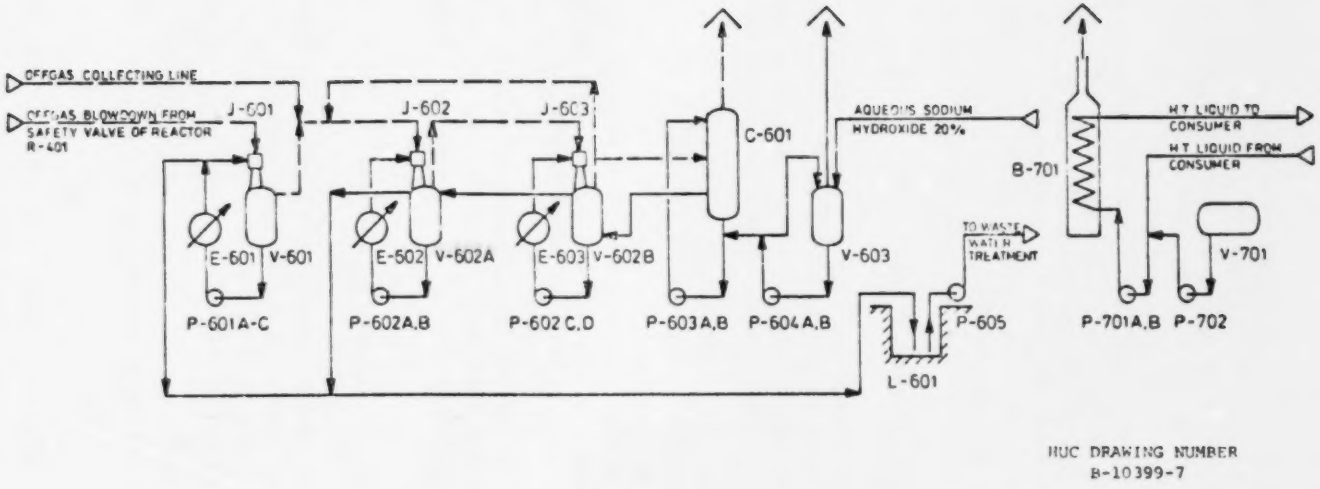

Figure 7. Emergency absorption and high temperature heating.

The unit consists of four stages with three liquid injection scrubbers connected in series, J-601, J-602, and J-603, followed by a scrubbing column, C-601. Each injection scrubber is provided with its own storage tank, V-601, V-602 A, and V-602 B and its own circulating pump P-601 A/B, P-602 A/B, and P-602 C/D. The scrubber column, C-601, is also provided with its own pump, P-603 A/B.

The absorption reactions are exothermic, therefore, three coolers, E-601, E-602, and E-603, are also provided.

The first stage for emergency absorption deals only with the treatment of gases released as a result of the opening of the reactor safety valve. The other waste vent gases are passed directly into the second stage via the suction of injector J-602. Those inerts and contaminate gases not yet absorbed are then fed through the vent line of the storage tanks to the suction of the third injector, and finally into the bottom of column C-601. Bypass is provided to avoid vacuum in storage tank V-601, resulting from the suction of injectors J-602 and J-603.

Depending on the NaOH required, it is possible to take a small amount of fresh NaOH from storage tank V-603 and feed it by means of pumps P-604 A/B into the bottom of scrubber C-601.

The NaOH flows via overflow control from the scrubbing column into V-602 B, then via overflow into V-602 A and from there into wastewater pit L-601.

Pit L-601 must also provide intermediate storage capacity for the larger amount of bleaching liquor to be treated in the wastewater purification plant. This provision is necessary in view of the fact that the capacity of the wastewater purification unit would not be sufficient in the case of instantaneous discharge of the NaOH from the emergency absorption tanks.

INCINERATION UNIT (See Figure 8)

In the combustion unit, those leftover residues generated from both the pretreatment of feedstock heavy ends and solvents and the bottom product of the HCl-column are destroyed. In addition, all wastewater streams containing traces of chlorinated hydrocarbons are incinerated. These aqueous wastes are obtained in small quantities during the pure CCl_4 distillation and in the pretreatment units for feedstock light ends, heavy ends, and solvents (see Figures 2, 3, and 6, and HUC Block Diagram Number B-10400-7 in Volume II).

Waste products (chlorinated hydrocarbons) are fed to a burner system, B-301 and B-302, designed for incinerating liquid and/or gaseous residues. An important factor to be considered in the incineration process is the caloric value of the waste products themselves. This depends primarily on chlorine content; a high chlorine content results in low caloric value and vice versa.

A chlorine content of 60-70% may normally be expected in the waste products from the production of vinyl chloride monomer, and the caloric value will be in the range of 2000 to 4000 kcal/kg. Complete combustion is unlikely when the caloric value is below 3000 kcal/kg. Additional fuel must,

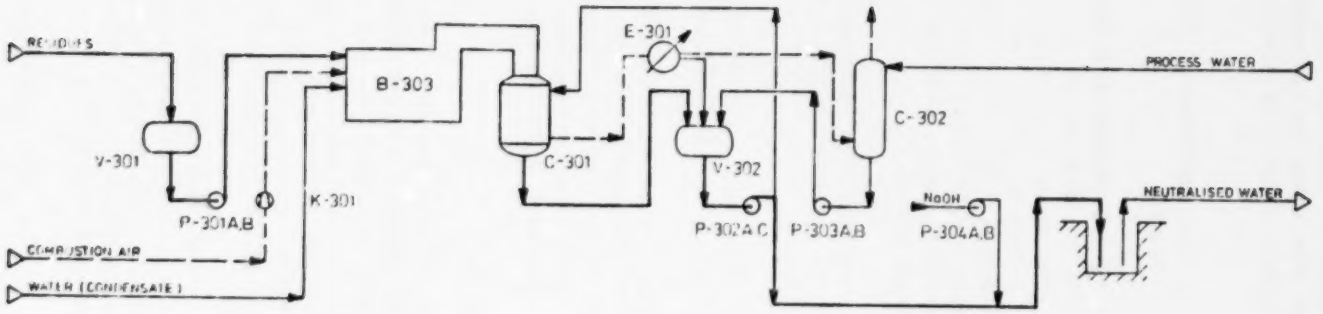

Figure 8. Incineration.

therefore, be used by providing a separate gas burner or by mixing fuel oil with the waste.

The waste, consisting of chlorinated hydrocarbons (C, H, Cl, O) possibly containing traces of Fe, Cu and Al compounds, is atomized with the aid of compressed air or steam in a special burner. Combustion air and water (e.g., wastewater) are also admitted to the combustion chamber. Incineration takes place at a pressure of about 2000 mm water head and at temperatures in the range of 1250°C.

The combustion product is a gaseous mixture of N_2, O_2, HCl, CO_2, Cl_2, and H_2O.

The equilibrium between water, chlorine, hydrogen chloride and oxygen in the incinerator gases can be expressed as follows:

$$H_2O + Cl_2 \rightleftarrows 2\ HCl + \tfrac{1}{2}\ O_2 \ .$$

Equilibrium constant:

$$Kp = \frac{(P\ HCl)^2 \cdot (P\ O_2)^{\frac{1}{2}}}{(P\ H_2O) \cdot (P\ Cl_2)} \ ,$$

where:
- P HCl = partial pressure of HCl in the reaction gas
- P O_2 = partial pressure of O_2 in the reaction gas
- P H_2O = partial pressure of H_2O in the reaction gas
- P Cl_2 = partial pressure of Cl_2 in the reaction gas.

The reaction is temperature dependent.

The ratio of hydrogen chloride to chlorine in the reaction gas mixture increases with rising temperature. Furthermore, the conversion (combustion) of chlorinated hydrocarbons is improved at higher temperatures.

Excessive oxygen and hydrogen also affect the reaction. A lack of oxygen in the reaction zone results in the formation of soot, whereas a great excess of oxygen tends to increase the free chlorine content in the exhaust gas. An excess of water suppresses the formation of free chlorine.

The reason for adding more water than required for the chemical equilibrium (hydrogen demand) is to reduce the combustion temperature from approximately 2000°C to approximately 1250°C to offer better protection to the firebrick lining of the combustion chamber, which will "melt" at or near 1500°C.

Combustion Chamber System

The following design criteria for the combustion chamber are important:

Temperature and residence time of the reactants in the combustion zone are critical parameters. High temperatures permit short residence times and vice versa, provided that complete combustion of the chlorinated hydrocarbons is assured. Complete combustion may be defined as having been achieved when the following parameter is greater than 99%:[2]

$$\frac{(CO_2 - CO)}{CO_2} \times 100$$

In this case, a large combustion chamber was designed similar to that used in the waste incineration process of Hoechst AG, ensuring complete combustion of the chlorinated hydrocarbons with minimum formation of free chlorine. These results are achieved by a long residence time ($\geq$ 3 seconds) of the reaction gases in the combustion zone and by introducing a relatively large quantity of water.

Combustion Gas Treatment

The hot combustion gases from the incineration chamber, B-303, are fed via a cooling tube to the quench system, C-301, where the gas temperature is lowered from about 1000°C to about 100°C by injecting recirculated hydrochloric acid. The cooling tube is bricklined. The quench column has an acid-proof lining to protect the steel wall against corrosion.

Quench gas is fed to column C-302 where the HCl is absorbed in "clean" water. Additional hydrochloric acid thus formed collects in the bottom and is sent partly to the quench acid collecting tank V-302, and partly to the neutralization pit. The recirculating hydrolochloric acid concentration is approximately 2.5% by weight.

SPECIAL INVESTIGATIONS

Feedstock

The bases for the feedstock composition calculations are the analyses performed by Repro Chemical Corporation in the report entitled "Converting Chlorohydrocarbon Wastes by Chlorolysis."[3] Based upon the Repro data, four residue mixtures had to be examined to cover the probable operating spectrum:

1. 60% by weight VCM residues and 40% by weight solvent wastes;
2. 100% VCM residues;
3. VCM residues and maximum oxygenated chlorinated hydrocarbons (HO); and
4. Minimum VCM residues and maximum solvent wastes (shown to be same as mixture 1).

Mixture 1 was considered as the "base case." The resulting feed compositions are summarized in Table 1. Based upon a sized design capacity of 25,000 MT/yr of feed mixture 1, allowable feed rates for mixtures 1 through 3 are presented in Table 2. For mixtures 1 through 3, detailed material balances were also calculated as shown in Figures 9 through 11.

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TABLE 1. COMPOSITION OF FEEDSTOCK

Components	Formula	Molecular Mass kg/Kmol	Boiling Point °C	LE*	HED*	Solvent*	VCM-Solv* 60% VCM 40% Solv	VCM* 33% LE 67% HED	VCM-HO* 95% VCM 5% HO
1. Chloroethylene (VCM)	C_2H_3Cl	62.50	-13.3	10.9	-	-	2.2	3.6	3.4
2. Chloroethane	C_2H_5Cl	64.52	13.1	3.8	-	-	0.8	1.3	1.2
3. Dichloroethylene	$C_2H_2Cl_2$	96.94	32-60.3	4.5	0.5	-	1.1	1.8	1.7
4. Trichloromethane	$CHCl_3$	119.38	61.7	9.9	-	-	2.0	3.3	3.1
5. Chlorobutadiene	C_4H_5Cl	88.54	59.4-68	14.5	2.7	-	4.0	6.6	6.3
6. Dichloroethane	$C_2H_4Cl_2$	98.96	57-84	30.4	2.2	-	6.9	11.5	10.9
7. Carbon Tetrachloride	CCl_4	153.82	76.5	16.9	0.7	-	3.6	6.0	5.7
8. Benzene	C_6H_6	78.11	80.1	6.2	-	-	1.2	2.0	1.9
9. Trichloroethylene	C_2HCl_3	131.39	87.2	2.9	-	-	0.6	1.0	1.0
10. Dichloropropane	$C_3H_6Cl_2$	112.99	69.7-120.4	-	1.7	-	0.7	1.1	1.0
11. Trichloroethane	$C_2H_3Cl_3$	133.42	74-113	-	56.6	-	22.7	37.9	36.0
12. Dichloropropene	$C_3H_4Cl_2$	110.97	77-112	-	2.7	-	1.1	1.8	1.7
13. Dichlorobutene	$C_4H_6Cl_2$	125.00	101-156	-	26.0	-	10.4	17.4	16.6
14. Trichloropropene	$C_3H_3Cl_3$	145.42	114-142	-	0.7	-	0.3	0.5	0.5
15. Chlorobenzene	C_6H_5Cl	112.56	132.2	-	2.8	-	1.1	1.9	1.8
16. Tetrachloroethane	$C_2H_2Cl_4$	167.85	130-146	-	2.3	-	0.9	1.6	1.5
17. Dichlorobenzene	$C_6H_4Cl_2$	147.00	172-179	-	1.1	-	0.4	0.7	0.7
18. Hexachloroethane	C_2Cl_6	236.74	186	-	-	25.0	10.0	-	-
19. Hexachlorobutadiene	C_4Cl_6	260.76	215	-	-	65.0	26.0	-	-
20. Hexachlorobenzene	C_6Cl_6	284.78	322	-	-	10.0	4.0	-	-
21. 2,4-Dichloro-Phenoxy-Acetic-Acid n-Butylester	$C_{12}H_{14}O_3Cl_2$	277.15	146 (1 mm Hg)	-	-	--	--	-	2.5
22. 2,4,5-Trichloro-Phenoxy-Acetic-Acid n-Butylester	$C_{12}H_{13}O_3Cl_3$	311.59			-	--	--	-	2.5
				Σ 100.0	100.0	100.0	100.0	100.0	100.0

*By weight.

TABLE 2. FEEDRATE

Components	Formula	LE*	HED*	Solvents*	VCM+Solv.* 60% VCM 40% Solv.	VCM* 33% LE 67% HED	VCM+HC* 95% VCM 5% HC
1. Chloroethylene (VCM)	C_2H_3Cl	67	-	-	67	113	106
2. Chloroethane	C_2H_5Cl	24	-	-	24	41	38
3. Dichloroethylene	$C_2H_2Cl_2$	28	6	-	34	56	53
4. Trichloromethane	$CHCl_3$	61	-	-	61	103	97
5. Chlorobutadiene	C_4H_5Cl	90	34	-	124	206	197
6. Dichloroethane	$C_2H_4Cl_2$	188	28	-	216	359	341
7. Carbon Tetrachloride	CCl_4	105	9	-	114	188	178
8. Benzene	C_6H_6	38	-	-	38	63	59
9. Trichloroethylene	C_2HCl_3	18	-	-	18	31	31
10. Dichloropropane	$C_3H_6Cl_2$	-	21	-	21	34	31
11. Trichloroethane	$C_2H_3Cl_3$	-	711	-	711	1184	1125
12. Dichloropropene	$C_3H_4Cl_2$	-	34	-	34	56	53
13. Dichlorobutene	$C_4H_6Cl_2$	-	326	-	326	544	519
14. Trichloropropene	$C_3H_3Cl_3$	-	9	-	9	16	16
15. Chlorobenzene	C_6H_5Cl	-	35	-	35	59	56
16. Tetrachloroethane	$C_2H_2Cl_4$	-	29	-	29	50	47
17. Dichlorobenzene	$C_6H_4Cl_2$	-	14	-	14	22	22
18. Hexachloroethane	C_2Cl_6	-	-	312.5	312.5	-	-
19. Hexachlorobutadiene	C_4Cl_6	-	-	812.5	812.5	-	-
20. Hexachlorobenzene	C_6Cl_6	-	-	125	125	-	-
21. 2,4-Dichloro-Phenoxy-Acetic-Acid n-Butylester	$C_{12}H_{14}O_3Cl_2$	-	-	-	-	-	78
22. 2,4,5-Trichloro-Phenoxy-Acetic-Acid n-Butylester	$C_{12}H_{13}O_3Cl_3$	-	-	-	-	-	78
	Σ	619	1256	1250	3125	3125	3125

*kg/h.

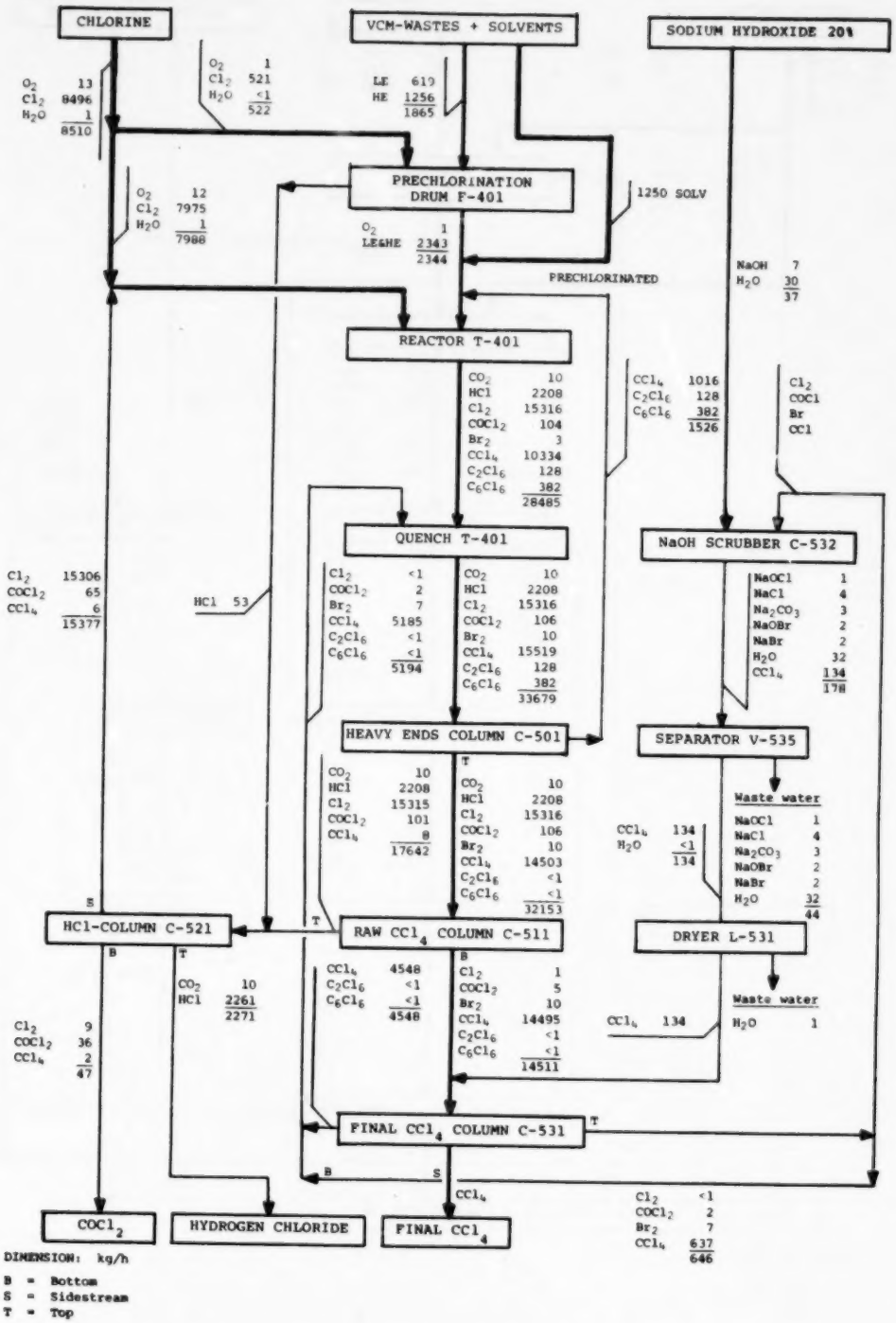

Figure 9. Chlorolysis plant for waste conversion, material balance (VCM-wastes + solvents).

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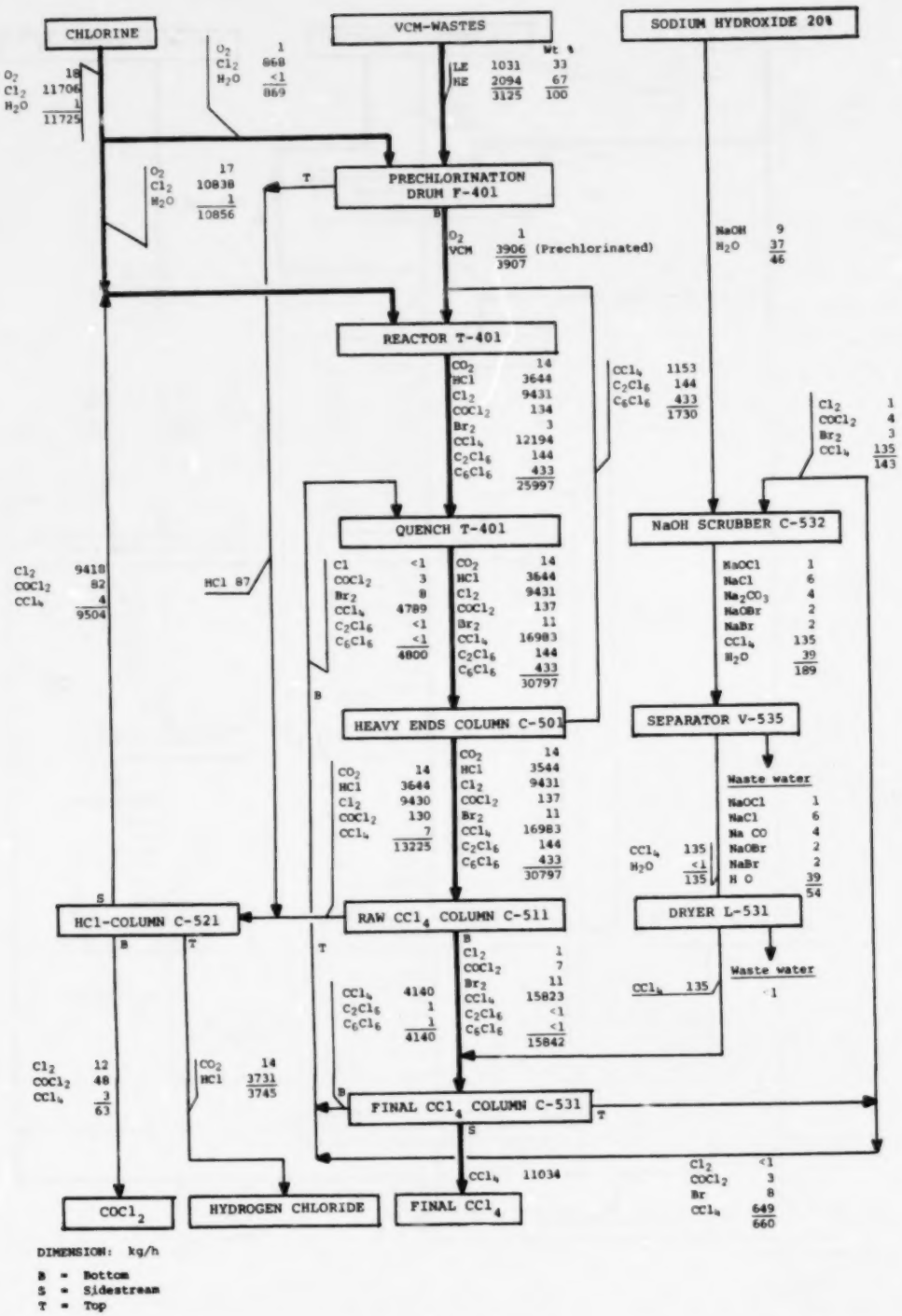

Figure 10. Chlorolysis plant for waste conversion, material balance (VCM-wastes).

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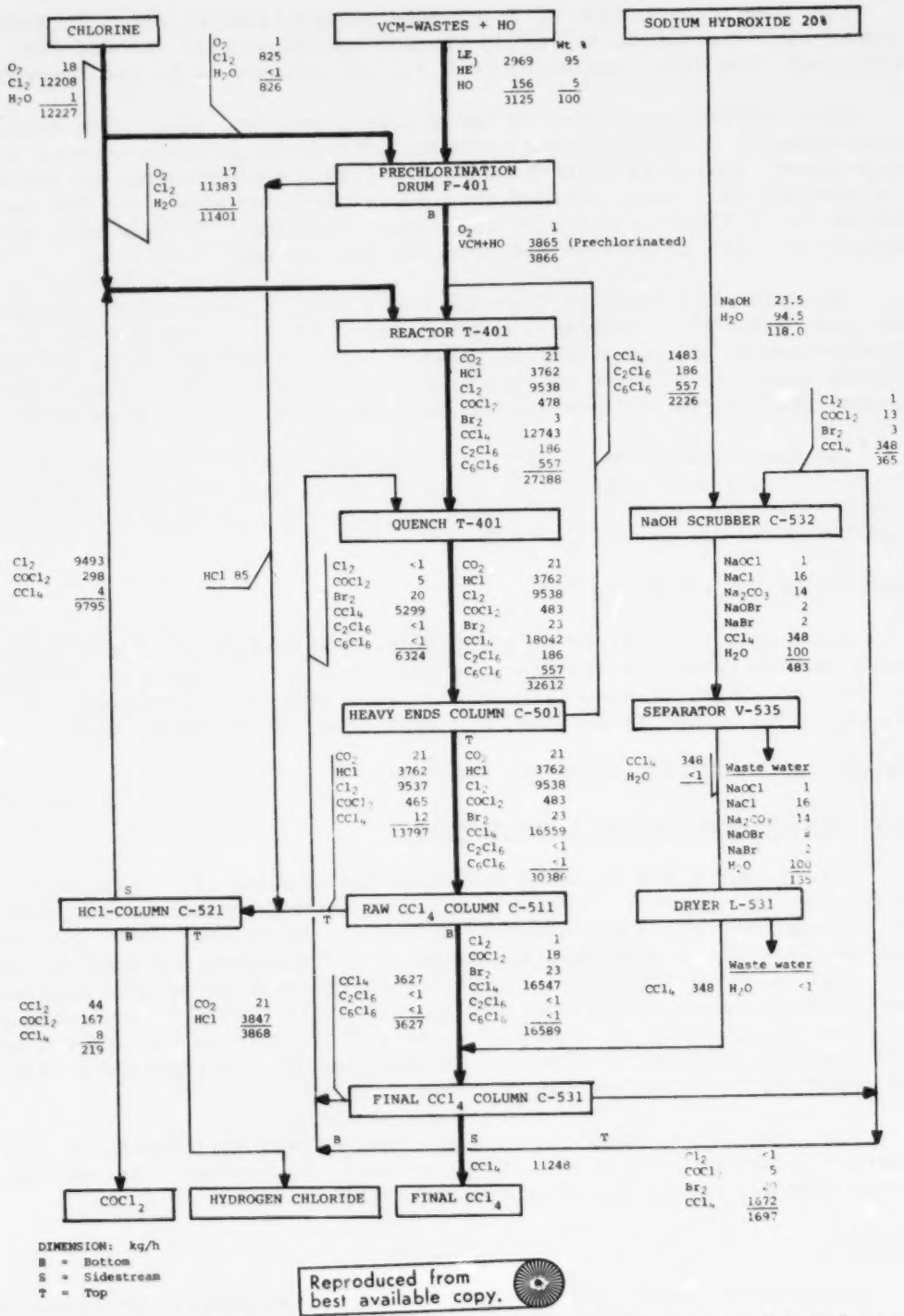

Figure 11. Chlorolysis plant for waste conversion, material balance (VCM-wastes + HO).

HUC Drawing No. B05543-3

For the composition of light ends as specified by Repro in Table 1, the numbers with two digits following the decimal point were rounded off and the difference from 100%, amounting to 0.2%, was assumed to be dichloroethane.

The unknown components of heavy ends distillate (HED) were calculated as trichloroethane. The undefined aromatic chlorocarbon components of 3.9% were apportioned into 2.8% chlorobenzene and 1.1% dichlorobenzene corresponding to the observed mass ratio between chloro- and dichlorobenzene in VCM residues of Hoechst AG, without considering the other aromatics. In this way, an aromatic content of 3.74% as benzene was obtained for the HED.

Moreover, in deviation from the Repro data, a bromine content of 0.2% in HED was assumed. Bromine results from rock salt and is taken up with the chlorine gas in the electrolysis process. In the production of dichlorethane, bromine compounds, higher boiling than EDC, are obtained. These compounds are concentrated in the VCM heavy ends and discharged together with them.

The concentration of sulfur and sulfur-containing compounds is limited to 25 ppm S in all feed residues in order to avoid accelerated corrosion of the nickel reactor tube. The resulting elemental compositions for the three feedstocks are summarized in Table 3.

CAPACITY OF THE PLANT

Plant design was based on a capacity of 25,000 MT/yr of chlorohydrocarbon waste residue feedstock mixture 1 as specified in the Special Investigations portion of this chapter with an on-stream time of 8000 hrs/yr. The rest of the year (760 hours) is provided for shut-down, maintenance, etc.

DISCUSSION OF DETAILED TECHNICAL FINDINGS

Base Case Residue Mixture 1 and Mixture 4

All equipment was designed and sized for mixture 1. According to the experience of Hoechst AG with various chlorohydrocarbon wastes, 40% will be the maximum solvents waste quantity which can be mixed with VCM residues. Mixture 1 is, thus, identical to mixture 4. The reason for this limitation is the high starting (chlorolysis initiation) temperature of this mixture in the reactor which is estimated to be approximately 200°C. Accordingly, feed chlorine would have to be heated up to 250°C. This is the upper limit based upon the materials of construction employed and the manufacture's limits for the high-pressure chlorine heat exchanger, E-402.

Also for this mixture--not yet having been experimentally examined--a chlorine excess of 180% of the stoichiometric requirement is calculated as being necessary to achieve proper conversions.

Mixture 2

Bottlenecks would result at the following points, in comparison with mixture 1, when using 25,000 MT/yr residues of mixture 2: prechlorination, HCl-column, and refrigerating unit. It was decided that it was more

TABLE 3. ELEMENTAL ANALYSIS OF FEEDSTOCKS (%)

Elements	VCM 33% LE 67% HED	VCM+Solv. 60% VCM 40% Solv.	VCM+HO 95% VCM 5% HO
C	27.9	23.5	29.0
H	3.3	2.0	3.4
Cl	68.7	74.4	66.7
Br	0.1	0.1	0.1
O	-	-	0.8
Σ	100.0	100.0	100.0

economical to utilize the reactor at 100% efficiency and to eliminate the bottlenecks in these other pieces of equipment.

For mixture 2, the required preheating temperature of the chlorine feed is about 120°C with an 80% chlorine excess.

Mixture 3

The material balance for case 3 shows 5% oxygenated residues (HO) added to VCM residues. It is not possible to mix a higher percentage of oxygenated residues (HO) since the content of aromatic calculated as benzene in the mixture would exceed the 5% experience limit.

The reason for this limit is the maximum permissible design temperature (620°C) of the reactor. For an aromatic content greater than 5% by weight, the final temperature would have to exceed 620°C to achieve the necessary conversions.

For mixture 3, an 80% excess chlorine is required with a preheating temperature of 120°C.

Treatment of Byproducts

The detailed material balances (see Figures 9 through 11) for the chlorolysis process show the amount of byproducts being produced.

The quality of HCl produced is sufficient for electrolysis and oxychlorination, but the HCl amount is too small to permit economical operation of such independent units in a waste complex of the capacity envisaged. Economic operation is possible only if HCl from other sources is available or if the amount of HCl chlorolysis can be added to existing electrolysis or oxychlorination plants.

Transporation of liquid HCl is permitted only in pressure vessels designed for a pressure of about 120 bar. Consequently, economical transport of large quantities is not possible over long distances. Therefore, it is recommended that the chlorolysis plant be sited within a corresponding production complex which can use the gaseous HCl produced by direct pipeline transfer.

The carbonyl chloride obtained in the bottom of the HCl-column is contaminated by chlorine and CCl_4. Carbonyl chloride has to be rectified, to allow for its usage as feedstock in an isocyanate process. Since the quantity obtained (36 kg/hr $COCl_2$) is very small, it is not economical to provide a separate column, a storage vessel with filling device, and all the safety facilities required for such a hazardous material. Thus, the stream taken from the bottom of the HCl column is passed directly to the residue combustion plant. Even when HO or similarly oxidized organic is mixed with the VCM residues, the quantity of carbonyl chloride is only 167 kg/hr. The purification of this $COCl_2$ would be economical only if the chlorolysis plant were built within a chemical complex, where the byproducts could be utilized by direct pipeline transfer.

PLANT DESIGN CONSIDERATIONS - PROCESS UNIT

Pretreatment of Residues

The residues as supplied cannot be used directly. The light ends, for example, contain up to 0.1% dissolved water, which must be eliminated by means of a silica gel adsorption drying plant.

Heavy ends and solvents contain mostly solid materials, e.g., soot, cocking products or polymers, which are not quantitatively converted to carbon tetrachloride and hydrogen chloride in the chlorolysis process. Because these components and non-volatile inorganic compounds accumulate in the reactor, they must be separated by filtration or, as in the case of solutions by distillation, e.g., in a falling-film evaporator. Non-volatile inorganic compounds like iron (III) chloride tend to be deposited in the bottom of the heavy ends column and are filtered out when the bottom product is recycled to the reactor.

When treating the solvents, it must be considered that the component hexachlorobenzene (HCB) contained in the residues is not completely soluble at ambient temperature. Therefore, this residue must be maintained at about 100-110°C in the hold tank to keep the HCB soluble.

The following conclusions are drawn for the design of equipment based upon the material balance for the base case as compared to those of the other mixtures, 2 and 3.

Drying of Light Ends (Unit 150)

The feed rate of light ends for mixture 2 amounts to 1031 kg/hr and for mixture 3, 980 kg/hr in comparison with 619 kg/hr for the base case. This corresponds to a capacity factor of 166% for operation with mixture 2 compared with the base case. The drier capacity is higher and designed for a feed rate of 2 m^3/hr light ends, since driers L-151 A/B are also designed for drying during start-up of the plant. Specified drier capacity is, thus, sufficient for both operations.

Treatment of Heavy Ends/Solvents (Unit 200/250)

Two falling-film evaporator units operated alternately are provided for operation with the base case mixture. The capacity for treating heavy ends is 1256 kg/hr and for solvents 1250 kg/hr so that the total capacity amounts to 2506 kg/hr. Both units can be used in parallel for operation with heavy ends (maximum 2094 kg/hr).

Reaction Part (Unit 400)

Prechlorination--

The light and heavy ends must be at first prechlorinated; however, the solvents can be directly fed into the reactor without prechlorination. For operation with mixture 2, the sum of the feed rates of light and heavy ends

into the prechlorinator amounts to 3125 kg/hr compared to 1875 kg/hr for the base case with required chlorine quantities of 869 kg/hr and 522 kg/hr, respectively. This means that the prechlorination quantity for the base case is too small by the factor of 166%.

In order to provide more flexibility when using all residue mixtures, the specified prechlorination equipment has been designed for mixtures 2 and 3.

Reaction--

In the reaction section, pumps P-401 A/B are designed for case 3, because the quantity of mixture 3 is 20% higher than in the base case. With regard to the feed rate, the capacity of reactor R-401 is sufficient for operation with all residue mixtures.

Separation Unit 500

The equipment in the distillation section has been laid out, in any case, according to the maximum load. Because of the high chlorine excess, the load in the heavy ends columns C-501 and in the crude CCl_4 column C-511 is maximum when mixture 1 is used. For mixtures 2 and 3, the HCl-column C-521 and pure CCl_4 column C-531 are loaded at a higher rate compared to the base case.

Incinerator (Unit 300)

The incineration unit is designed for mixtures 2 and 3 with a feed capacity of 600 kg/hr and an on-stream time of 8000 hrs/yr. Mixtures 2 and 3 provide the maximum residual wastes from the pretreatment units.

It is necessary to add water to wastes with a high heating value in order to regulate the reaction temperature in the combustion chamber. For this reason, most of the small waste water streams (shown in Figures 2, 3, and 6, and HUC Drawing Number B-10400-7, Volume II) containing traces of chlorinated hydrocarbons are used togehter with additional "clean" water to control the reaction temperature in the incinerator.

The off-gas is treated by scrubber C-302 operating with "clean" water. In case of perfect combustion, no free chlorine is formed and HCl can be removed thoroughly with water to meet emission standards.

In case of imperfect or incomplete conbustion, i.e., with too much excess oxygen, 500 (weight) ppm of chlorine may be obtained in the vent gas if washed only with water. To meet emission standards and to prevent this high chlorine content at the stack exhaust, the following provisions were made:

1. the stack height was fixed at 40 m, and

2. a small amount of caustic soda was specified to be added to the washing water to eliminate the traces of chlorine and HCl. Thus, a chlorine content of less than 20 (weight) ppm is expected.

Based upon these specifications and assumptions, i.e., a chlorine content at stack exit less than 20 weight ppm, a stack height of 40 m, and an allowable ground level concentration of 0.1 mg/m^3, the emission standards will not be exceeded up to a wind velocity of 0.1 m/sec. The calculations were checked using the nomograph in Figure 12.[3] According to the lengthy experience of Hoechst AG in operating incineration plants, no high boilers such as HCB and others will be detectable in the vent gas if the indicated design and operating specifications are followed.

The HCl acid produced (approximately 2.5 weight %) in the vent scrubber system is neutralized in a pit and then sent to battery limits for discharge as waste salt water.

Design Specifications

Detailed specifications for raw materials, utilities, auxiliaries, products, etc., were developed by combining Hoechst operating experience (Federal Republic of Germany) with American-Gulf Coast area chemical systhesis industry needs and experience. The resulting design values are presented in detail in Appendix A.

ENVIRONMENTAL WORK

Introduction

From a variety of industrial chlorination processes, e.g., vinyl chloride and chlorinated solvent and pesticide production, toxic and hazardous byproduct residues are obtained which have to be disposed of. Today, the disposition of these wastes has become a serious environmental, social, and even potentially a health problem. Industry is now forced by environmental and safety regulations to produce as little waste as possible, and then to have this waste treated with minimum impact on the environment. For this reason, industry strives to convert its wastes into products that may be utilized again, whenever and wherever it is possible.

Several processes for disposal of chlorinated residues by conversion to other products have been applied at commercial scale:

1. Incineration with scrubbing where muriatic acid is produced, from which part of the hydrogen chloride may be recovered (chlorine value);
2. A catalytic cracking process taking place in conjunction with the oxychlorination process (to produce vinyl chloride precursor) in which the hydrogen chloride of the combustion gas is consumed and converted to ethylene dichloride (recovers some chlorine and carbon values); and

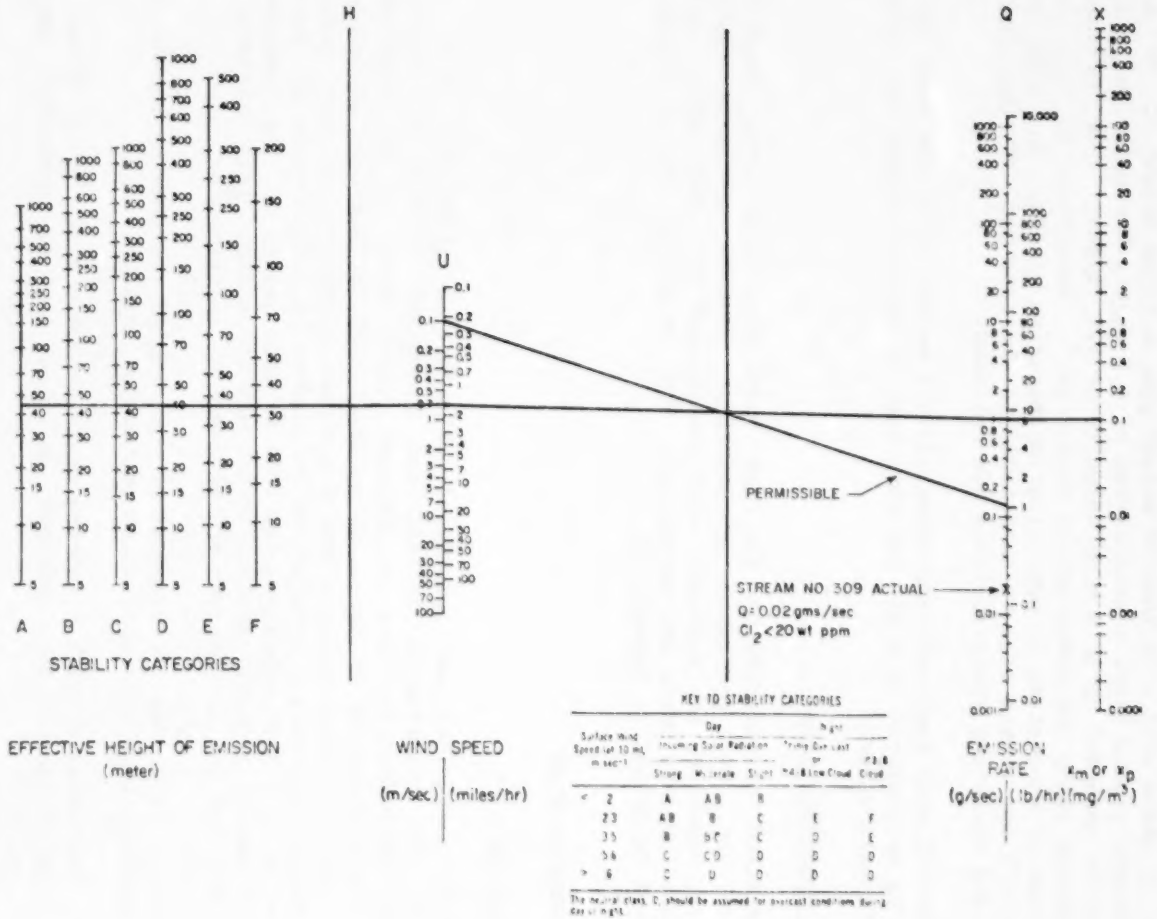

Figure 12. Correlation of chlorine emission rates and maximum ground level concentration.

3. The chlorolysis process, where carbon tetrachloride and anhydrous hydrogen chloride are produced recovering virtually all the carbon chlorine, and hydrogen values.

Chlorolysis Process

Chlorolysis is a recycling process for which byproduct residues of various chlorination processes may be used as feed in order to convert them into products that may be utilized again, that is, to carbon tetrachloride and anhydrous hydrogen chloride (which can also be absorbed in water and sold as muriatic acid).

This study is based on feedstock residues obtained from VCM-production and the production of solvents containing chlorine, e.g., perchloroethylene.

Chlorolysis itself produces only a small quantity of byproducts, since the space time yield and the conversion (95%) are highly efficient. All chlorolysis byproducts, that is those components which have not been completely converted to HCl and CCl_4, are recycled to the reactor to extinction. Carbonyl chloride is obtained as an unwanted byproduct if the feedstocks contain oxygen. Carbonyl chloride is burnt together with those blowdown tars that are left over from pretreatment of the feedstock residues.

The chlorolysis plant is provided with an absorption unit for the removal of chlorine and hydrogen chloride gas in case of emergency and for normal startup and shutdown of the plant. This unit consists of three stages, which assures that the environment remains unaffected.

Incineration Unit

As described previously, all pretreatment chlorinated tars that cannot be used in chlorolysis are burnt, together with all wastewater streams contaminated with traces of chlorinated hydrocarbons.

During incineration, HCl, CO_2, and H_2O are formed and, in case of improper functioning of the unit, also traces of chlorine. The hydrogen chloride is absorbed from the off-gas in a way that the environmental regulations are observed (See Figure 8).

For specification of the stack height, a Cl_2 or HCl concentration value for off gases from the absorber C-302 was assumed which was unfavorable by a factor of 10. According to the nomograph contained in an EPA report entitled "Estimation of Permissible Concentration of Pollutants for Continuous Exposure,"[3] using the specified stack height of 40 m, the actual value emission rate Q = 0.58 g/sec (with a safety factor of 10) was still below the permissible value Q = 1 g/sec.

SECTION 7

ECONOMIC ANALYSIS

1. The costs and economics presented herein are based on a new plant location with a clear and level site in the Gulf Coast area. It is also assumed that foundations can be installed with conventional spread footings and that a pumping station is not required to provide cooling water to the plant.

2. The basis of a new plant location significantly affects the economics of the chlorolysis plant. It should be recognized that the economic criteria presented in this study would be improved substantially if the chlorolysis plant were installed as part of an existing chlorocarbon chemical production complex.

3. The study is based on plant erection during the first half of 1977. No forward escalation has been included for possible increased or decreased costs from that time. It is estimated that approximately two and one-half years would be required to erect the plant from the time of contract award.

4. The economic criteria is based on a plant location that would be central and convenient to those plants producing vinyl chloride monomer and chlorinated solvent wastes. This condition exists in both the New Orleans and Houston areas. In either case the collection and transportation of the waste to the regional chlorolysis plant would be minimal.

5. The cost summaries presented in Tables 4 and 5 correspond to operation at the design feed capacity for the base (mixture I) and 100% VCM residue (mixture II) feed cases, respectively. Nominal values for both the carbon tetrachloride selling price and residue disposal toll charge of $300/MT and $75/MT, respectively, were assumed for these analyses.

6. The sensitivity of plant economics to assumed carbon tetrachloride value and toll charge for each feed case is summarized in Table 6 and plotted in Figures 12 and 13. The assumed carbon tetrachloride value ranged from $275/MT to $325/MT. Based on a cursory examination of the projected market, this range seems appropriate, but a more detailed analysis would be necessary at a later date for a precise economic evaluation. Similarly, the assumed toll charge range was $25/MT to $125/MT. As seen from Figures 12 and 13, the plant economics are not as sensitive to toll

TABLE 4. ECONOMIC EVALUATION SUMMARY
Base Case (Mixture 1) Feed Residues

BASIS 25,000 MT/yr 75,000 MT/yr CCl_4 Product

Total Fixed	$25,496,900
Process Royalty	3,500,000
Working Capital	2,549,690
Total Fixed Royalty & Working	$31,546,590

Raw Materials	Annual Quantity	Unit Price	Annual Cost
Cl_2	68,000 MT	$125/MT	$ 8,480,000
Caustic (20%)	14,500 MT	$30/MT	435,000
Methane	134,500,000 ft^3	$2/1000 ft^3	269,000
		Total Raw Material Cost	$ 9,184,000

Utilities			
Power	25,600,00 KWH	$0.015/KWH	$ 383,000
Steam (HP + LP)	52,000 MT	$4/MT	208,000
Cooling Water	3.9 x 10^9 gal.	$0.01/1000 gal.	39,000
		Total Utility Cost	$ 630,000

Operating Cost	Men/Shift	Total	
Labor	10	44	$ 761,000
Supervision			97,000
Maintenance, 4% Fixed			1,020,000
		Total Operating Cost	$ 1,878,000

Overhead Expense		
Direct Overhead	30% Labor & Supervision	$ 258,000
General Plant Overhead	50% Operating Cost	939,000
Insurance, Property Taxes	1.5% Total Fixed	381,000
Depreciation	10% BLCC & 5% Offsite	2,175,000
Interest	10% Working Capital	255,000
	Total Overhead	$ 4,008,000
	Process Royalty Over Ten Years	$ 350,000
	Total Production Cost for First Ten Years	$16,050,000

Product Credit	Annual Quantity	Unit Price	Annual Income
CCl_4	75,000 MT	$300/MT	$22,500,000
HCl	17,850 MT	$50/MT	892,500
		Product Credit	$23,392,500

TABLE 4. ECONOMIC EVALUATION SUMMARY (continued)
Base Case (Mixture 1) Feed Residues

Waste Credit	Annual Quantity	Unit Price	Annual Income
(Toll for Waste Removal)			
Chlorocarbon Waste	25,000 MT	$75/MT	$ 1,875,000
		Total Product & Waste Credit	$25,267,500
		GROSS INCOME	$ 9,217,500
		AFTER TAX INCOME	$ 4,608,750
		DEPRECIATION	$ 2,175,000
		CASH FLOW	$ 6,783,750
ROI	(After Tax Income) / (Total Fixed + Work)	16.4%*	
ROR	(Cash Flow) / (Total Fixed + Work)	24.2%	
Payout	(Total Fixed) / (Cash Flow)	3.75 yrs	

*These percentages are based on royalty paid over ten-year period after which return/rate would improve.

TABLE 5. ECONOMIC EVALUATION SUMMARY
100% VCM Residue Feed (Mixture II)

BASIS 25,000 MT/yr 88,500 MT/yr CCl_4 Product

Total Fixed	$25,496,900
Process Royalty	3,500,000
Working Capital	2,549,690
Total Fixed Royalty & Working	$31,546,590

Raw Materials	Annual Quantity	Unit Price	Annual Cost
Cl_2	93,800 MT	$125/MT	$11,750,000
Caustic (20%)	14,500 MT	$30/MT	435,000
Methane	134,500,000 ft^3	$2/1000 ft^3	269,000
		Total Raw Material Cost	$12,454,000

Utilities			
Power	25,600,000 KWH	$0.015/KWH	$ 383,000
Steam (HP + LP)	52,000 MT	$4/MT	208,000
Cooling Water	3.9 x 109 gal.	$0.01/1000 gal.	39,000
		Total Utility Cost	$ 630,000

Operating Cost	Men/Shift	Total	
Labor	10	44	$ 761,000
Supervision			97,000
Maintenance, 4% Fixed			1,020,000
		Total Operating Cost	$ 1,878,000

Overhead Expense		
Direct Overhead	30% Labor & Supervision	$ 258,000
General Plant Overhead	50% Operating Cost	939,000
Insurance, Property Taxes	1.5% Total Fixed	381,000
Depreciation	10% BLCC & 5% Offsite	2,175,000
Interest	10% Working Capital	255,000
	Total Overhead	$ 4,008,000
	Process Royalty Over Ten Years	$ 350,000
	Total Production Cost for First Ten Years	$19,320,000

Product Credit	Annual Quantity	Unit Price	Annual Income
CCl_4	88,500 MT	$300/MT	$26,550,000
HCl (100%)	30,000 MT	$50/MT	1,500,000
		Product Credit	$28,050,000

TABLE 5. ECONOMIC EVALUATION SUMMARY (continued)
100% VCM Residue Feed (Mixture II)

Waste Credit	Annual Quantity	Unit Price	Annual Income
(Toll for Waste Removal)			
Chlorocarbon Waste	25,000 MT	$75/MT	$ 1,875,000
		Total Product & Waste Credit	$29,925,000
		GROSS INCOME	$10,605,000
		AFTER TAX INCOME	$ 5,302,500
		DEPRECIATION	$ 2,175,000
		CASH FLOW	$ 7,477,500
ROI	$\frac{\text{(After Tax Income)}}{\text{(Total Fixed + Work)}}$	18.9%*	
ROR	$\frac{\text{(Cash Flow)}}{\text{(Total Fixed + Work)}}$	26.7%*	
Payout	$\frac{\text{(Total Fixed)}}{\text{(Cash Flow)}}$	3.4 yrs	

*These percentages are based on royalty paid over ten-year period after which return/rate would improve.

TABLE 6. SUMMARY OF RESULTS OF ECONOMIC CALCULATIONS FOR BASE AND MIXTURE II (100% VCM Residue) Feed Cases

Selling price CCl_4, $/MT	Toll charge waste, $/MT	ROI, %	ROR, %	Payout, yrs	Discounted cash flow, %
BASE CASE					
275	75	13.1	20.7	4.4	13.0
300	75	16.4	24.2	3.8	16.0
325	75	19.7	27.5	3.3	18.2
275	25	10.9	18.6	4.9	-
300	25	14.2	21.9	4.1	-
325	25	17.5	25.4	3.6	-
275	125	15.3	23.1	3.9	-
300	125	18.6	26.5	3.4	-
325	125	22.0	29.7	3.1	-
MIXTURE II (100% VCM Residue) CASE					
275	75	14.9	20.5	4.0	15.0
300	75	18.9	24.5	3.4	18.0
325	75	22.9	28.4	3.0	21.0
275	25	12.5	20.5	4.4	-
300	25	16.7	24.5	3.7	-
325	25	20.6	28.4	3.2	-
275	125	17.2	25.0	3.6	-
300	125	21.1	28.9	3.1	-
325	125	25.1	32.8	2.8	-

charge as carbon tetrachloride price. Nevertheless, it would be necessary to negotiate contracts for these charges with waste producers before proceeding with construction of a regional chlorolysis plant.

As can be seen from these calculations, the adjustments to the economics analysis which may be necessary for a specific location or situation can be either additive or deductive. In general, it can be expected that all of these factors would tend to balance out. Therefore, the net result is such that the economics, as presented herein, are sufficiently accurate and representative to be used for future planning purposes.

With regard to the results of this analysis, if one uses the nominal carbon tetrachloride value and toll charge above, it can be seen that the return on investment (ROI) ranges from about 16% to 19%. Similarly, the rate of return (ROR), which includes credit for depreciation, corresponds to approximately 24% to 27%. Finally, the discounted cash flow is in the range of 16% to 18% for the same conditions. (Return on investment and rate of return are defined in Tables 4 and 5.)

REFERENCES

1. Disposal of Organochlorine Wastes by Incineration at Sea. EPA-430/9-75-104, U.S. Environmental Protection Agency.

2. Shiver, J. Converting Chlorohydrocarbon Wastes by Chlorolysis. Repro Chemical Corporation. EPA-600/2-76-270, U.S. Environmental Protection Agency, Washington, DC.

3. Handy, R. and A. Schindler. Estimation of Permissible Concentrations of Pollutants for Continuous Exposure. Research Triangle Institute. EPA-600/20-76-155, U.S. Environmental Protection Agency, Research Triangle Park, NC. 1975.

APPENDIX A

DESIGN SPECIFICATIONS

SPECIFICATIONS OF RAW MATERIALS, UTILITIES AND AUXILIARIES

Raw Materials

Chlorine (liquid)	
Chlorine	99.5% minimum
Water	<60 wt ppm
Nitrogen trichloride	unknown
Hydrogen	<50 wt ppm
Oxygen	<1500 wt ppm
Carbon dioxide	<5 wt ppm
Mercury	negligible

Note: This specification was given by Repro[3] and was used as the basis for all material balances. It would be preferable to use chlorine with a maximum 20 ppm H_2O and 50 ppm O_2.

Utilities

Steam--

Steam (high pressure) saturated	BL	200 psig
Steam (low pressure) saturated	BL	15 psig

Cooling Water--

Supply

Temperature, summer conditions	90°F
Pressure	60psig
Return	100°F
Pressure	to be set by pressure drop of users
Fouling factors	0.0002-0.005 $\frac{hr \cdot ft^2 \cdot {}^\circ F}{BTU}$
	0.0004-0.001 $\frac{m^2 h\, {}^\circ C}{kcal}$

Fuel

Natural Gas--

The United Gas Pipeline Company of Jackson, Mississippi, would provide natural gas for the facility. The specification for this gas is as follows:

Fuel Value - 1.035-1.039 BTU/cf--

Hydrogen	5% by mol.
Oxygen	0% by mol.
Carbon monoxide	0% by mol.
Carbon dioxide	0.82% by mol.
Methane	96.13% by mol.
Propane	0.27%
Nitrogen	0.31%
Ethane	2.32%
Isobutane	0.06%
n-Butane	0.06%
Pentane	0.03%
H_2S 0%	
Sulphur	0.01 g/100 cf
Humidity	<7 lbs/1,000,000 cf
Pressure	60 lbs delivered
NGPA charcoal test	0 gal./1,000,000

Electric Power--

Conditions at the BL of the plant:

1. Frequency: 60 Hz
2. Power receiving voltage: 13.800 kV
3. Equipment voltage: 500 V and 13.800 kV
4. Lighting circuit voltage: 208 V
5. Short circuit capacity on the side 13.8 kV: 200 MVA
6. Feeding of power and lighting users from common transformers
7. Voltage of electric motors Capacity up to 200 kW: 500 V
   Larger than 200 kW: 13,800 V
8. Voltage variation from nominal not more than $\pm$ 5%, in case of emergency $\pm$ 10%
9. Frequency variation: $\pm$ 1%, in case of emergency $\pm$ 5%
10. Emergency power will be supplied to maintain safety operation or execute safe shutdown

Nitrogen--

Oxygen content	maximum 20 wt ppm
Oil content	absent
Dew point	-55°C
Pressure	35 psig
CO_2 content	not detectable

Plant Air--

Pressure	85 psig
Dew point	-9°C (during summer)
Oil content	absent

Instrument Air--

Pressure	85 psig
Dew point	-30°C
Oil	absent

Auxiliaries

Ammonia--

Conditions at BL, tank storage or bottles.

Caustic Soda--

Conditions at BL	30% or 50% by wt
Pressure	50 psig

Silica Gel

Specifications--

SiO_2	99.8% by wt
Si_2O_3	0.01%
Al_2O_3	0.03%
TiO_2	0.03%
Na_2O	0.02%
CaO	0.04%
Traces of other elements	0.04%

Physical Properties--

Specific gravity	2.2 g/cm^3
Bulk density	750 g/l
Specific surface	800 m^2/g
Size	3-4 mm

Heat Transfer Medium - Dowtherm A--

Boiling point	575°F
Melting point	-18°F
Density, lb/ft^3 at boiling point	55

Refrigerant	R-12

Local Potable Water

(Henry Speir, Laboratory Technician, National Aeronautics and Space Administration, Bay St. Louis, MO, 601/688-2000. 9 June 1976.)

Analysis	ppm
Silica	19.00
Iron 0.02	
Manganese	0.10
Calcium	3.70
Magnesium	0.50
Sodium	91.00
Potassium	1.10
Bicarbonate	194.00
Carbonate	11.00
Sulfate	17.00
Chloride	12.00
Fluoride	0.30
Nitrate	0.60
Dissolved solids	252.00
Total phosphorus	50.00

Tripen (Hexachlorobutadiene)

As lubricate for chlorine high pressure pump P-402 and heating agent for reboiler E-522.

Specification	Technical Grade
Molecular weight	260.8
Specific gravity at 20°C, kg/l	1.68
Melting point, °C	-18
Boiling point at 760 mm Hg, °C	212
Specific heat at 22°C, kcal/ck°C	0.202
Viscosity, cp, 15°C	9.22
Viscosity, cp, 21°C	3.68
Viscosity, cp, 50°C	2.40
Viscosity, cp, 98°C	1.13
Thermal conductivity at 22°C, kcal/mhr °C)	0.087

PRODUCT SPECIFICATION

Final Product

Specification--

Carbon tetrachloride	minimum 99.9% by wt
Impurity (maximum)	
Humidity	35 ppm wt
Free chlorine	10 ppm wt

Non-volatile residue	6 ppm wt
Acidity (HCl)	10 ppm wt
Trichloroethylene	100 ppm wt
Perchloroethylene	50 ppm wt
Hexachloroethane	10 ppm wt
Other additions	100 ppm wt
(by gas chromatography)	
Maximum color	5 APHA
Iodine index	negative
Specific weight at 25°C	1.582-1.590
Distillation limits	not more than 1°C

Byproduct

Hydrogen Chloride (gaseous)--

Analysis	
HCl	minimum 99% by wt
Impurities (maximum)	
Chlorine	100 ppm wt
Carbon tetrachloride	50 ppm wt
Carbonyl chloride	50 ppm wt
Moisture	100 ppm wt

WASTE STREAMS (See Figures 2, 3, and 6 of Volume I)

Waste Gas (Stream Numbers refer to HUC Drawing Number B-10400-7 in Volume II)

Stream Number	Amount, kg/h	Composition
206	6	leakage air, traces of heavy ends
255	6	leakage air, traces of solvents
309	2851	inerts 96 wt %
	maximum 4334	H_2O 4 wt %
605	1250	inerts
		Cl_2 maximum 10 vol. ppm
		$COCl_2$ maximum 10 vol. ppm
		CCl_4 maximum 10 vol. ppm
538	10	inerts
		CCl_4 maximum 50 wtr ppm
		$COCl_2$ maximum 1 wt ppm
		HCl maximum 3 wt ppm
607	7475	N_2 72.9 wt %
		H_2O 10.6 wt %
		O_2 3.7 wt %
		CO_2 12.8 wt %
		SO_2 0.4 wt ppm

Waste Water (Stream Numbers refer to HUC Drawing Number B-10400-7 in Volume II)

313	14,000	NaCl 5 wt %		
			Normal	Maximum
606	normal 40	H_2O	90 wt %	80 wt %
	maximum 50,000 in case of emergency	NaOH	5-10 wt %	16 wt %
		NaOCl	2 wt %	1 wt %
		NaCl	2 wt %	1 wt %
		Na_2CO_3	<<0.1 wt %	0.1 wt %
		CCl_4	-	0.8 wt %
		Heavy ends	-	0.2 wt %

CONSUMPTION FIGURES

The expected consumption figures for raw materials, chemicals, and utilities for the chlorolysis and incineration plant, based upon 1,000 kg of feedstock residues, are as follows:

Raw Materials and Chemicals

Chlorine (100%)	2723 kg (base case)
	3943 kg (maximum, case III)
NaOH (20%)	580 kg

Utilities

Power	640 kWH
Cooling water, $\Delta t = 5^{o}C$	580 m^3
Steam, 15 psig	1150 kg
Steam, 200 psig	960 kg
Natural gas, 9210 kcal/Nm^3)	152 Nm^3
Nitrogen	16 Nm^3
Instrument air	654 Nm^3
Atomizing air	160 Nm^3
Condensate	0.15 m^3
Process water	4 m^3

The above utility figures do not include minor consumption in the auxiliary units such as waste HCl treatment or cooling tower operation, etc.

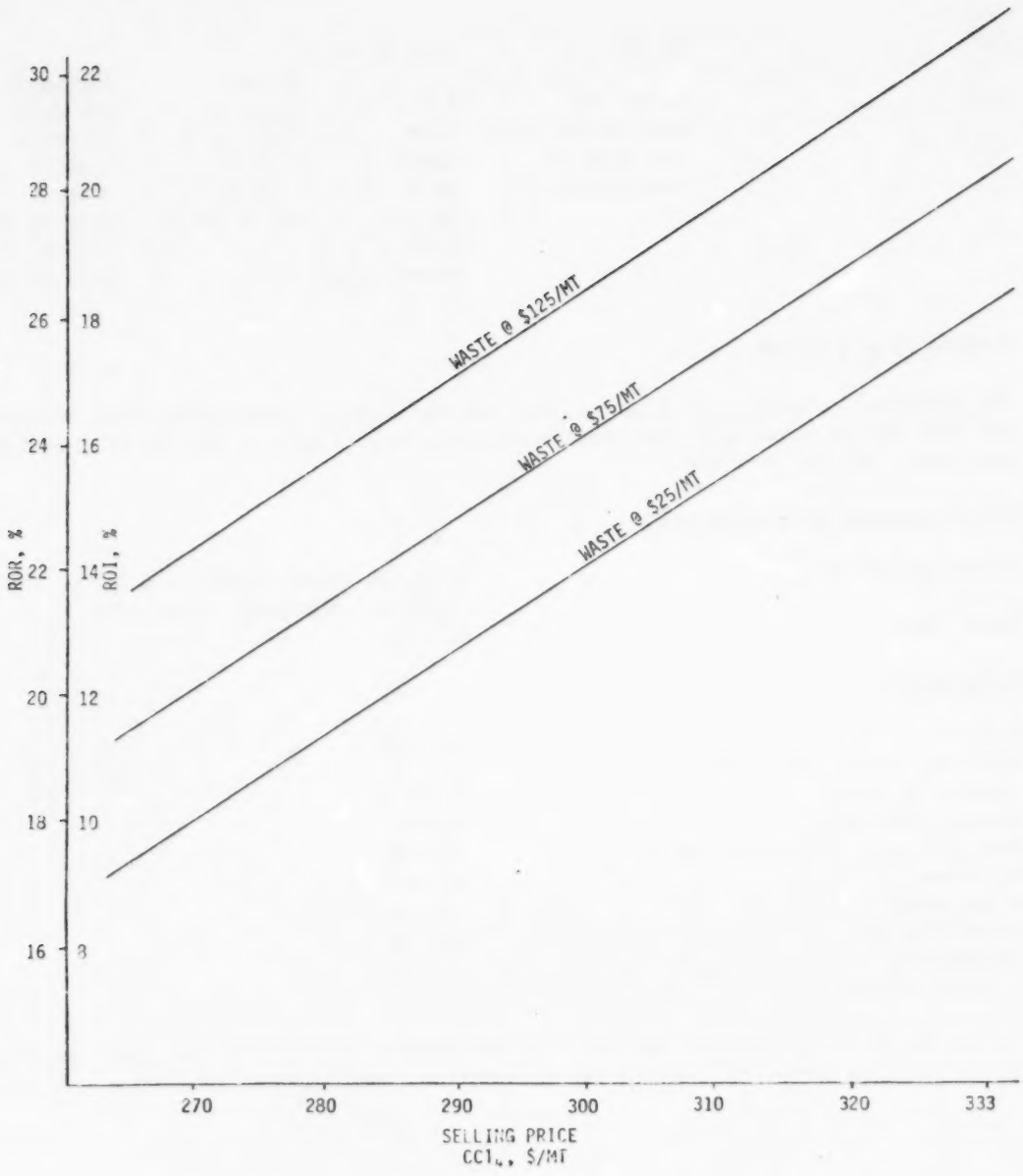

Figure A-1. Sensitivity of chlorolysis plant economics to carbon tetrachloride price and disposal toll charge (base feed mixture).

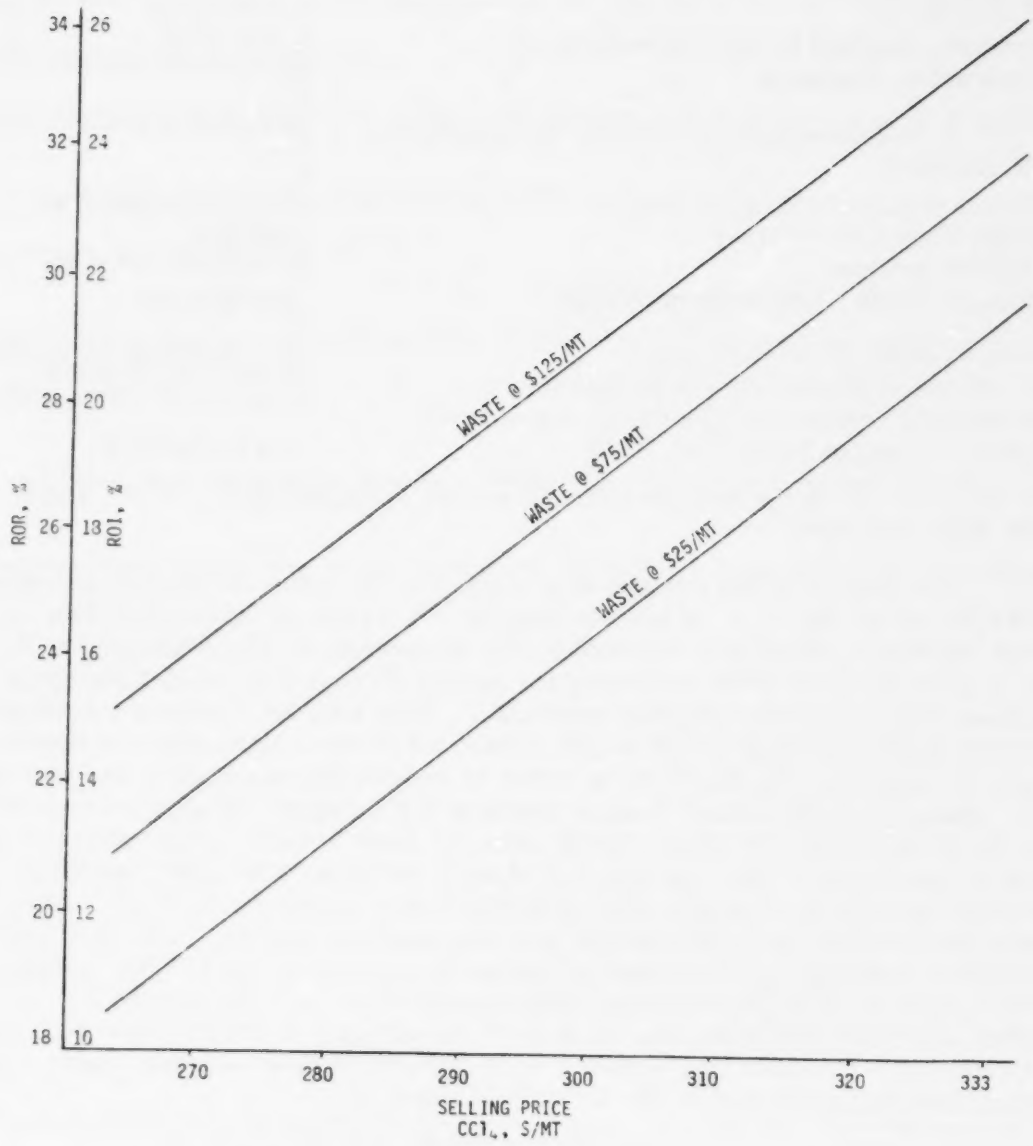

Figure A-2. Sensitivity of chlorolysis plant economics to carbon tetrachloride price and disposal toll charge (100% VCM residue feed).